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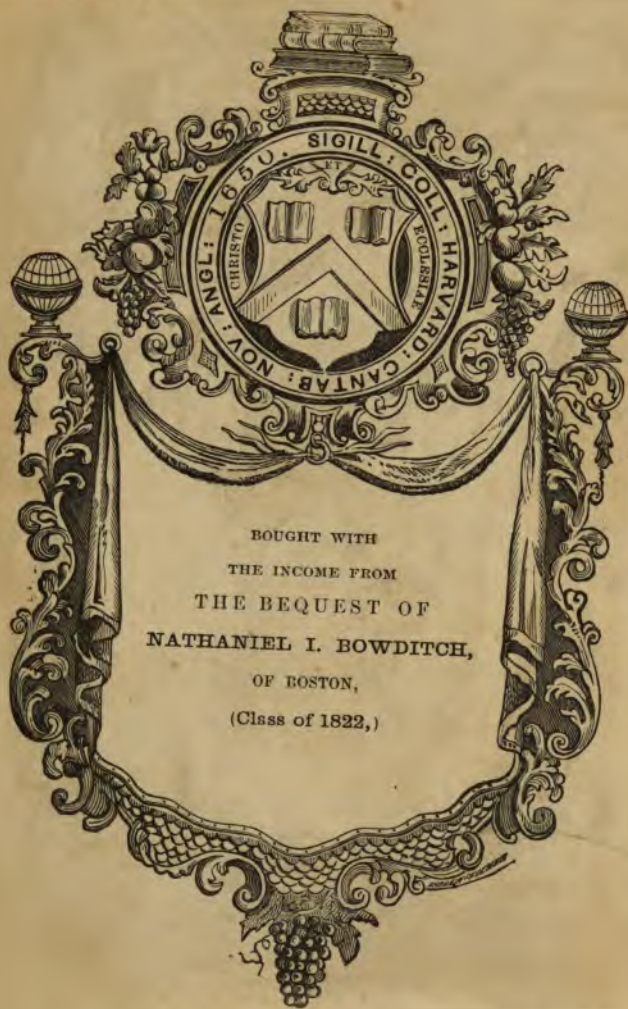
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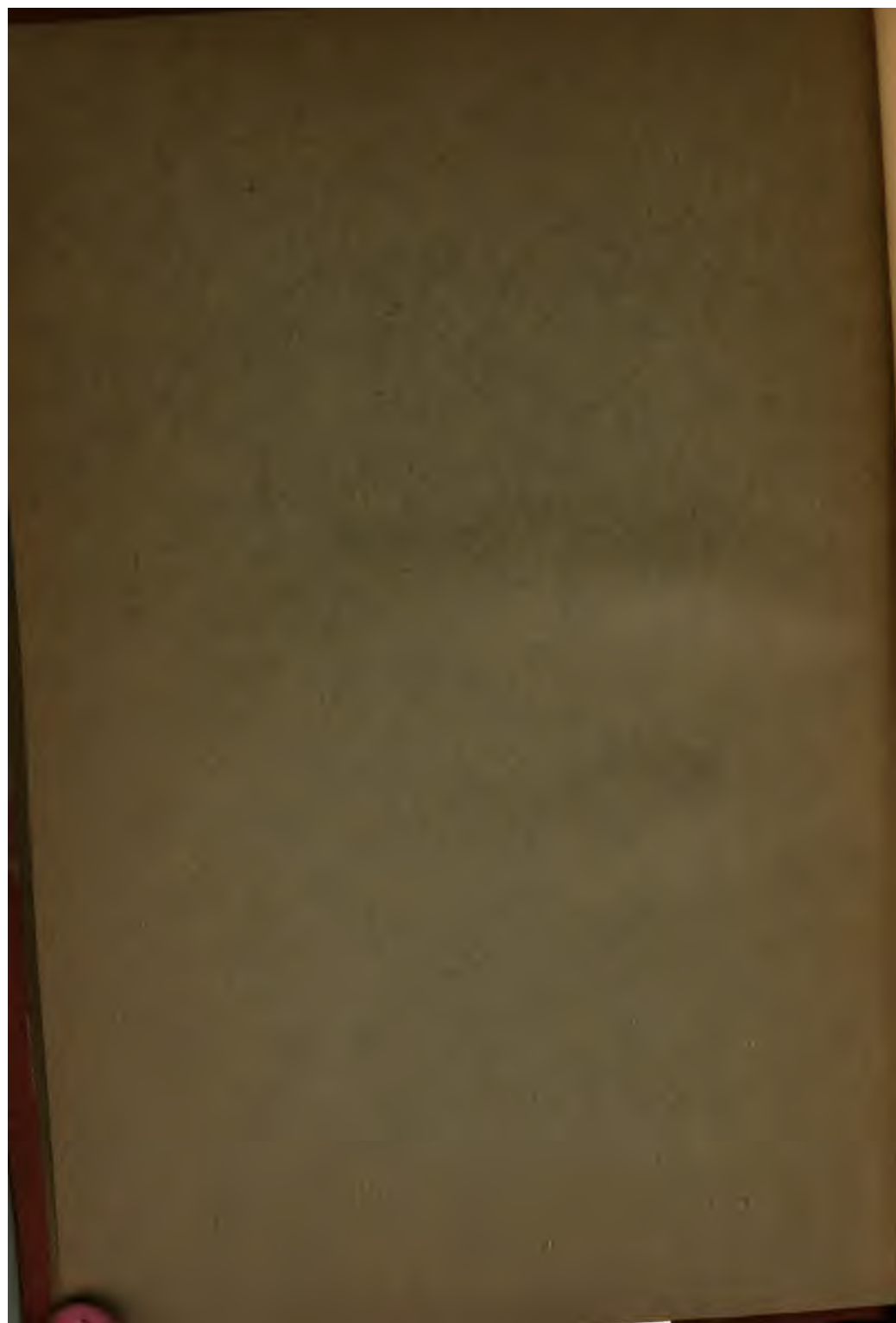
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ELECTRO-CHEMICAL
ANALYSIS.

SMITH.

⊙

ELECTRO-CHEMICAL ANALYSIS.

BY

EDGAR F. SMITH,

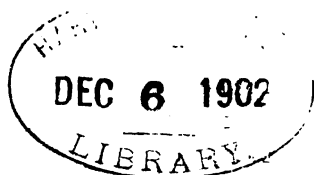
PROFESSOR OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA.

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With Thirty-nine Illustrations.

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1902.

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PREFACE.

The first edition of this book appeared twelve years ago (1890). It was published then because the writer, after many years of experimentation, was convinced that the electric current had proved its right to be classed as a reagent in the quantitative determination and separation of metals. To-day the number of text-books relating to electro-chemical analysis, to the preparation of inorganic and organic compounds in the electrolytic way, and to the various theories of electrolysis has become quite large. There is scarcely a laboratory, where chemical analysis is taught, or where it is applied, in which use is not made of the "subtile agent" of Faraday.

Since the appearance (1894) of the second edition, as well as its German (1895) and French (1900) translations, numerous additions have been made to the domain of which the book especially treats; so that it was concluded to thoroughly revise the entire text. In doing this the author has abstained from any attempt to present the prevalent theories on electrolysis, the purpose of the book being of a wholly different character, and, furthermore, because these theories have been exhaustively treated in a masterly manner in special volumes readily accessible to all students of chemistry.

The present edition differs greatly from its predecessors. Among the very first changes will be observed the de-

scription of an electro-chemical laboratory. This laboratory has been the outgrowth of a real demand and cannot fail to be suggestive and perhaps helpful to persons who purpose making an installation for electrolytic work. A few alterations have been made in the historical section, but the great changes will appear in the sections devoted to the determination and separation of the metals. Many of the earlier directions in reference to the determination of the individual metals have been omitted and more reliable and definite conditions substituted for the same. The section devoted to separations has been entirely recast, each separation being given in all of its possible forms with conditions that experience has demonstrated will yield satisfactory results.

The new illustrations scattered here and there through the text have been made from photographs taken by Mr. Walter T. Taggart, Sc.B., to whom the author's thanks are here expressed. It is also a great pleasure to acknowledge indebtedness to the many students who, through a period of years, have with readiness and skill tested methods of determination and separation, time after time, as the writer has suggested.

S.

THE JOHN HARRISON LABORATORY
OF CHEMISTRY.
1902.

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ABBREVIATIONS.

AM. CH.	=	<i>The American Chemist.</i>
AM. CH. JR.	=	<i>American Chemical Journal.</i>
AM. JR. SC. AND AR.	=	<i>American Journal of Science and Arts.</i>
AM. PHIL. SOC. PR.	=	<i>Proceedings of the American Philosophical Society.</i>
ANN.	=	<i>Annalen der Chemie und Pharmacie.</i>
BER.	=	<i>Berichte der deutschen chemischen Gesellschaft.</i>
BERG-HÜTT. Z.	=	<i>Berg- und Hüttenmännische Zeitung.</i>
B. S. CH. PARIS	=	<i>Bulletin de la Société Chimique de Paris.</i>
CH. NEWS	=	<i>Chemical News.</i>
CH. Z.	=	<i>Chemiker-Zeitung.</i>
C. R.	=	<i>Comptes Rendus.</i>
DING. P. JR.	=	<i>Dingler's Polytechnisches Journal.</i>
ELEKTROCH. Z.	=	<i>Elektrochemische Zeitschrift.</i>
G. CH. ITAL.	=	<i>Gazetta chimica italiana.</i>
JAHRB.	=	<i>Jahresbericht der Chemie.</i>
J. AM. CH. S.	=	<i>Journal of the American Chemical Society.</i>
JR. AN. CH.	=	<i>Journal of Analytical and Applied Chemistry.</i>
JR. F. PKT. CH.	=	<i>Journal für praktische Chemie.</i>
JR. FR. INS.	=	<i>Journal of the Franklin Institute, Phila.</i>
M. F. CH.	=	<i>Monatsheft für Chemie.</i>
PHIL. MAG.	=	<i>Philosophical Magazine.</i>
WIED. ANN.	=	<i>Wiedemann's Annalen.</i>
Z. F. A. CH.	=	<i>Zeitschrift für analytische Chemie.</i>
Z. F. ANG. CH.	=	<i>Zeitschrift für angewandte Chemie.</i>
Z. F. ANORG. CH.	=	<i>Zeitschrift für anorganische Chemie.</i>
Z. F. ELEKTROCHEM.	=	<i>Zeitschrift für Elektrochemie.</i>
Z. F. PH. CH.	=	<i>Zeitschrift für physikalische Chemie.</i>

ELECTRO-CHEMICAL ANALYSIS.

INTRODUCTION.

Many chemical compounds are decomposed when exposed to the action of an electric current. A decomposition of this kind is called *electrolysis*, while the substance undergoing change is termed an *electrolyte*. The products of the decomposition are the *anions* and *cations*, or those (1) which separate at the *anode*, the positive electrode or pole (+ P), and (2) those separating at the *cathode*, the negative electrode or pole (— P) of the source of the electric energy.

This behavior of compounds has become of great service to the analyst, inasmuch as it has enabled him to effect the isolation of metals from their solutions, and by carefully studying the electrolytic behavior of salts it has been possible for him to bring about quantitative determinations and separations.

The electrolytic method of analysis is especially inviting, since it permits of clean, accurate, and rapid determinations where the ordinary methods yield unsatisfactory results. This statement is readily confirmed on recalling the gravimetric methods usually employed in the estimation of copper, mercury, cadmium, bismuth, tin, etc., etc. That this assertion may be the conviction

of every student of analysis, the writer would call attention, first, to the course of the current in solutions of some of the more frequently occurring salts; after which will follow a brief account of the various modes of obtaining the electric current, how it may be measured, and how controlled. Finally, all the metals which have been studied electrolytically will be taken up in detail, and their various determinations will be followed by a number of separations to show how widely the electrolytic method of analysis may be applied.

1. ACTION OF THE ELECTRIC CURRENT UPON ACIDS AND SALTS.

			At the - Pole.	At the + Pole.
Hydrochloric acid	+ the current	=	Hydrogen	+ Chlorine.
Copper chloride	+ " "	=	Cu	+ Cl ₂ .
Zinc chloride	+ " "	=	Zn	+ Cl ₂ .
Nitric acid	+ " "	=	H	+ NO ₂ + O.

In this last case the hydrogen further acts upon more nitric acid and produces ammonia (NH₃) and water.

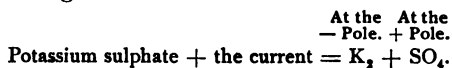


The oxygen liberated here attacks a second molecule of lead nitrate, and produces lead peroxide, $\text{Pb}(\text{NO}_3)_2 + \text{O}_2 = \text{PbO}_2$, which deposits upon the positive electrode.

			At the - Pole.	At the + Pole.
Copper nitrate	+ the current	=	Cu	+ (NO ₂) ₂ .
Sulphuric acid	+ " "	=	H ₂	+ SO ₄ .

Secondary changes frequently occur in these decompositions; thus, in the last example the SO₄ reacts with the water present: $\text{SO}_4 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{O}$, the oxygen going to the positive electrode. In the electrolysis of

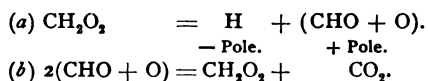
copper sulphate, which is analogous to sulphuric acid, secondary changes also occur.



In this decomposition the liberated potassium acts upon water, with the liberation of hydrogen and the formation of potassium hydroxide.

Bourgoin observed the following changes with formic, acetic, and oxalic acids, and their salts:—

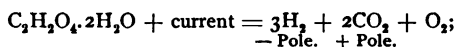
1. *Formic Acid*.—The decomposition may be expressed in two equations—



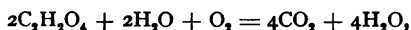
The decomposition of sodium formate yields carbon dioxide and formic acid at the anode, and hydrogen and sodium hydroxide at the cathode.

2. *Acetic Acid*.—The electrolysis of the dilute acid affords hydrogen at the negative electrode, and at the positive electrode a mixture of oxygen, carbon dioxide, and a small quantity of carbon monoxide. Consult also *Z. f. ph. Ch.*, 33, 108.

3. *Oxalic Acid*.—The electrolysis of this acid with a current obtained from four Bunsen cells gave decompositions which may be expressed as follows:—

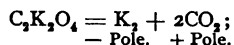


the oxygen reacts upon additional acid:—

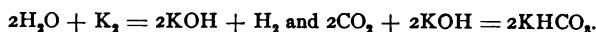


so that the final products are pure carbon dioxide at the positive electrode and hydrogen at the opposite pole.

The decomposition of potassium oxalate may be formulated in the following way:—



the liberated metal and the carbon dioxide then react further:—



When exposed to the same influence ammonium oxalate yields hydrogen at the negative electrode, and hydrogen ammonium carbonate at the positive electrode. The latter compound further breaks down into ammonia and carbon dioxide.

Succinic acid is electrolyzed with difficulty. In its decomposition the products which have generally been observed at the positive electrode were oxygen and the two oxides of carbon. Its electrolytic oxidation in a divided cell gave as products: tartaric acid, oxalic acid, aromatic bodies, oxygen, carbon monoxide, carbon dioxide, ethylene and methane (J. Am. Ch. S., **21**, 967). By electrolyzing sodium succinate Kekulé obtained hydrogen at the cathode, and carbon dioxide and ethylene at the anode.

Tartaric acid + the current gave at

— Pole.

+ Pole.

hydrogen

acetic acid, carbon dioxide,
carbon monoxide, and oxygen;

while with potassium tartrate the products were hydrogen and potassium at the cathode and acid potassium tartrate, carbon dioxide, carbon monoxide, and oxygen at the anode. An alkaline solution of potassium tartrate gave hydrogen at the cathode and at the anode, acetic acid, the oxides of carbon, oxygen, and ethane (C_2H_6).

In the case of potassium cyanide the products are potas-

sium hydroxide and hydrogen at the cathode with cyanogen at the anode. The cyanogen does not appear there in gas form, but as an isomeride, paracyanogen. As the quantity of the latter increases, the liquid, surrounding the anode, acquires a yellow to brownish-yellow color. The paracyanogen separates from this apparent solution spontaneously in black, amorphous floccules. (Hittorf, *Z. f. ph. Ch.*, 10, 616; also 12, 97.) Also consult page 53.

The above examples will suffice to indicate the nature of the decomposition due to the current; they will assist very materially in understanding the changes occurring in ordinary electrolytic analyses. For further particulars in this direction, consult Tommasi's *Traité Théorique et pratique d'Électrochimie*, although the statements there made will in many instances require revision in the light of more recent investigations.

2. OHM, VOLT, AND AMPERE.

These terms may be defined as follows:—

The *ohm* is the unit of resistance. Its value is represented by a column of mercury 1 sq. mm. in cross-section, and 106.2 cm. in length at the temperature 0° C.

The *volt* is the unit of electromotive force (E. M. F.). It is the E. M. F. which gives a current of one ampere through a resistance of one ohm.

The *ampere* is the unit of current. It is the current which, under an electromotive force of one volt, flows through a circuit offering a resistance of one ohm.

$$A = \frac{V}{O}; \text{ or better, } C = \frac{E}{R}.$$

3. SOURCES OF THE ELECTRIC CURRENT.

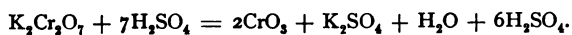
The electric energy required for quantitative analysis has been variously furnished by batteries of well-known types, magneto-electric machines, dynamos, thermopiles, and electrical accumulators or storage cells. A brief description of some of these may be properly introduced here.

The *Grenet* cell or *Bichromate Battery* (Fig. 1) consists of two plates of carbon (K) and one of zinc (Z), movable by

FIG. 1.



means of the handle, *a*. This is a convenient arrangement, as it allows of easy interruption of the current. The liquid to be used in this cell consists of potassium bichromate (1 lb.), strong sulphuric acid (2 lbs.), and water (12 lbs.). In mixing these, the probable chemical change is:—



The chemical action in the cell, when the current passes, may be expressed by the equation:—



The writer found four cells of this type (capacity two quarts) very serviceable in the electrolysis of solutions of cadmium, uranium, molybdenum, and other metals. No disagreeable fumes arise from cells of this class. The

FIG. 2.

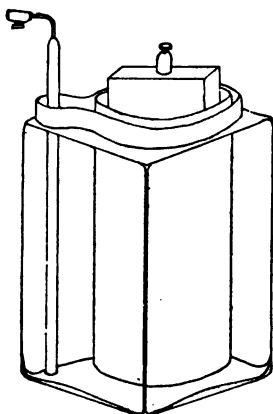
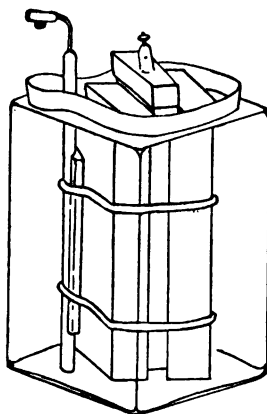


FIG. 3.



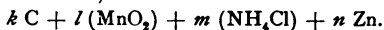
electromotive force is about two volts, and the internal resistance low. The Grenet cell loses in intensity when used for long periods, but regains its value when it has remained out of action for some time.

Leclanché Cell (Figs. 2 and 3).—Two forms of this cell are in use. In the first, to the left of the figure, there is a zinc rod, immersed in a solution of ammonium chloride, and a carbon plate inside a porous cup, tightly packed with a mixture of manganese dioxide and broken gas carbon. The porous cup is only intended to hold the

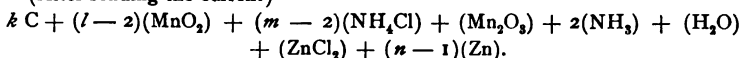
mixture in position. There is but one liquid, and that a strong solution of ammonium chloride. The *E. M. F.* of this cell equals 1.47 volts; it decreases rapidly when sending strong currents. It is inferior to the Daniell cell when a steady current is desired for a long period.

The chemical action in cells of this kind Ayrton expresses as follows:—

(Before sending the current)—



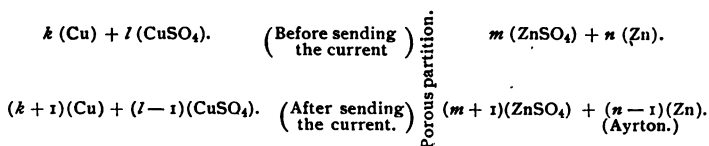
(After sending the current)—



The letters *k*, *l*, *m*, *n* represent indefinite amounts of the acting substances.

In the modified Leclanché cell the porous cup is not needed, as compressed prisms of manganese dioxide, gas carbon, and shellac are used around the carbon plate.

The *Daniell* cell (Fig. 4) consists of a glass jar, the porous cup T, and a cylinder of zinc (Z), the negative pole. Outside of the porous cup is the sheet-copper cylinder K. The zinc is the negative electrode, and the copper the positive electrode. The zinc stands in dilute sulphuric acid (1 : 20), and the copper in copper sulphate. Zinc sulphate often replaces the sulphuric acid. The chemical action in the cell is probably:—



The *E. M. F.* of this cell is about 1.07. The *Meidinger* (Fig. 5) and *Crowfoot* (Fig. 6) cells are modifications of the

Daniell, and very serviceable in electrolytic work when currents of low intensity are desired. In the sketch of the

FIG. 4.

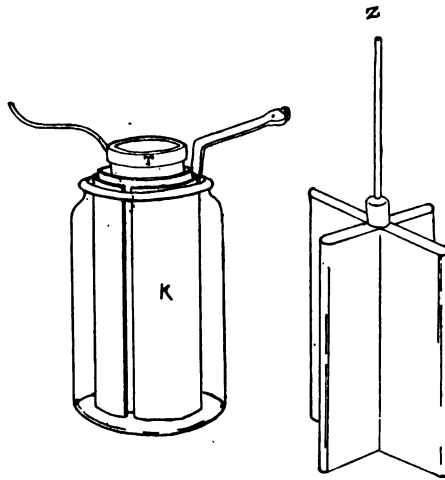


FIG. 5.

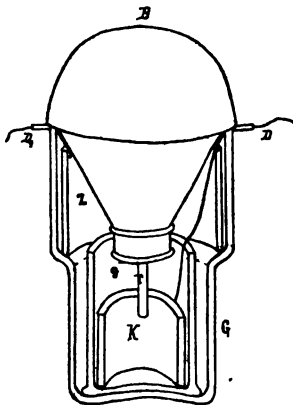
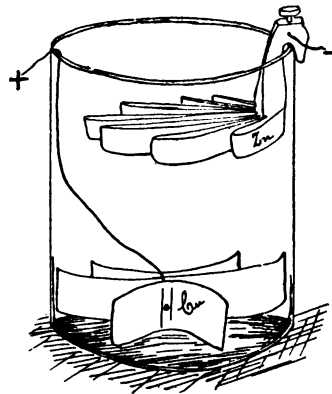


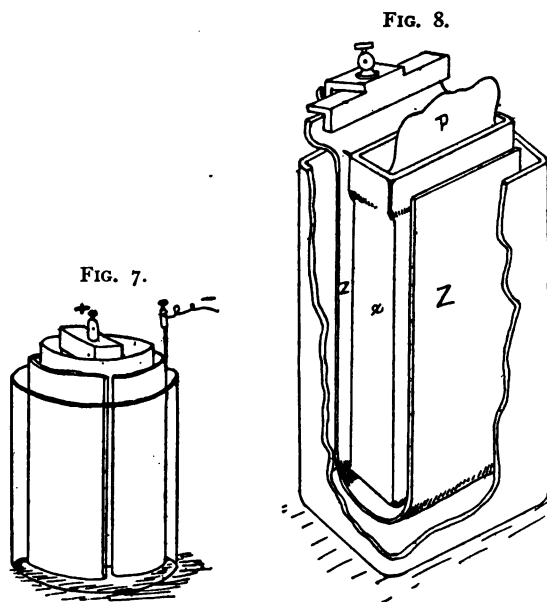
FIG. 6.



Meidinger cell, *G* is a large glass jar; *g*, a small glass vessel, in which stands the copper cylinder, *K* (+ *P*). *Z* (— *P*)

is a cylinder of zinc. B contains the supply of copper sulphate crystals.

The current from either of these batteries remains quite constant for long periods. The cells themselves do not require much attention. Half a dozen of either of these forms will do nearly all the electrolytic work of an ordinary laboratory. The "Crowfoot" form can be readily and

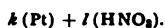


cheaply prepared. Rejected acid bottles, after removing the neck and upper portions, answer well as jars.

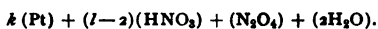
If currents of greater *E. M. F.* are required, the Bunsen (Fig. 7) or Grove cell (Fig. 8) should be used. In the former there is zinc in dilute sulphuric acid, or a mixture of potassium bichromate and sulphuric acid, and a carbon plate in a cup of nitric acid. It is a less expensive cell

than the Grove, as platinum is not employed. It is not so readily handled, and consumes more nitric acid. Its electromotive force is somewhat less than that of the Grove form. In the latter there is a strip of platinum (P) in concentrated nitric acid (in the porous cup, x), and zinc (ZZ) in dilute sulphuric acid (one pint of acid and ten pints of water). The *E. M. F.* is 1.93 volts. When acting, nitrogen tetroxide is set free; this can be in a measure suppressed by adding ammonium chloride to the nitric acid. The chemical changes occurring in the Bunsen and Grove cells are very similar. Ayrton expresses them as follows:—

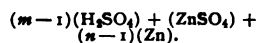
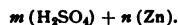
(Before current is sent)—



(After sending current)—



Porous partition.



The internal resistance of the Grove cell is small. To obtain good results both the Bunsen and Grove cells require constant attention.

In amalgamating the zincs in any of the preceding batteries, first allow them to remain over night in very dilute hydrochloric acid, then immerse in mercury, and with a wet cloth rub the latter into the metal. This should be done once a week, when the cells are in daily use.

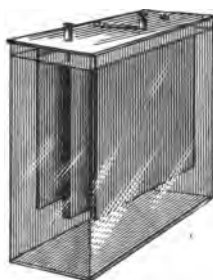
The *Cupron* cell (Fig. 9) consists of two amalgamated zinc plates, between which is suspended a porous copper oxide plate. The liquid used in this cell is an 18 per cent. solution of commercial caustic soda. The *E. M. F.* is 0.85 volt. The liquid should cover the plates completely. In case of prolonged use a layer of paraffin oil is

placed on the surface of the solution to exclude the carbon dioxide of the air as much as possible. This form of battery will be found very useful for general electrolytic purposes.

For further information upon batteries, consult Ayrton's *Practical Electricity*.

Magneto-electric machines and dynamos have been used to some extent in electrolytic decompositions, but a detailed description of their construction will not be given. It will be sufficient to add that a dynamo with a tension

FIG. 9.



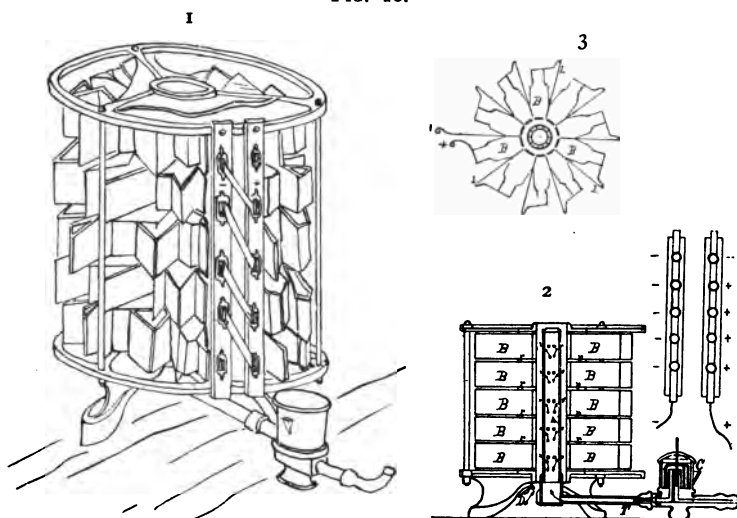
of 5 volts will answer for about all the determinations, separations, and oxidations which are carried out electrolytically. See further Smith's *Oettel's Electrochemical Experiments*, pp. 27-37, P. Blakiston's Son & Co., Philadelphia.

Thermopiles have also been used to furnish currents for electrolytic work. Their use has been objected to upon the ground that the currents afforded by them are rarely strong enough for the greater number of determinations and separations, and again they are easily broken

and difficult to repair. The forms generally met with are those recommended by Clamond and Noë.

The Clamond thermopile is pictured in Fig. 10. 1 is a perspective view of the same; 2 represents a vertical section, and 3 a basal section, showing the bars and armatures. The elements consist of bars of a zinc and antimony alloy and a strip of sheet-iron. These are arranged in circles, as indicated in 3; they are placed one above the

FIG. 10.



other. In 3, *B* represents the bars of zinc and antimony alloy, while the tinned sheet-iron plates are marked *L*. The sheet-iron serves to conduct the current from one element to the other; hence, these strips rest upon the bars *B*. Heat expands the latter, and in consequence renders the contact more intimate. The single elements, as well as the circles of elements, are separated from each other by plates of asbestos (see *r* in 2). The cylinder itself

consists of a series of such circles. The welded points of the bars are all directed to the centre of the cylinder. The gas flames are prevented from coming in immediate contact with them by the asbestos lining of the cylinder. As gas is employed to furnish the necessary heat, in the middle of the cylinder will be observed a clay tube (*A*) provided with apertures (2 and 3). The gas enters through the Giroud regulator *C* (1 and 2), which makes it possible to maintain a uniform temperature and a constant current. From *C* it is conducted to *A*, through *T*, into which air is admitted by suitable apertures. The mixture of air and gas burns at the openings in *A*. Additional air is supplied through *D*. Light the gas jets from above, after removing the cover. The poles of each ring of elements end in binding screws, thus enabling the operator to connect any number of them, depending upon the external resistance (*Z. f. a. Ch.*, 15, 334). When in excellent condition, these thermopiles are said to yield a current equivalent to 400–500 c.c. of oxyhydrogen gas per hour. The form of thermopile recently devised by Gülcher (*Z. f. ang. Ch.* (1890), Heft 18, 548; *Electrotechnische Zeitschrift*, 11, 187) possesses marked advantages over the types just described. It is decidedly more durable. The largest form (Fig. 11) consumes hourly 170 litres of gas and develops an electromotive force of 4 volts, with an internal resistance of 0.6–0.7 ohm. Those who have used this modified thermopile consider it extremely valuable in charging storage cells for use in electro-chemical analysis.

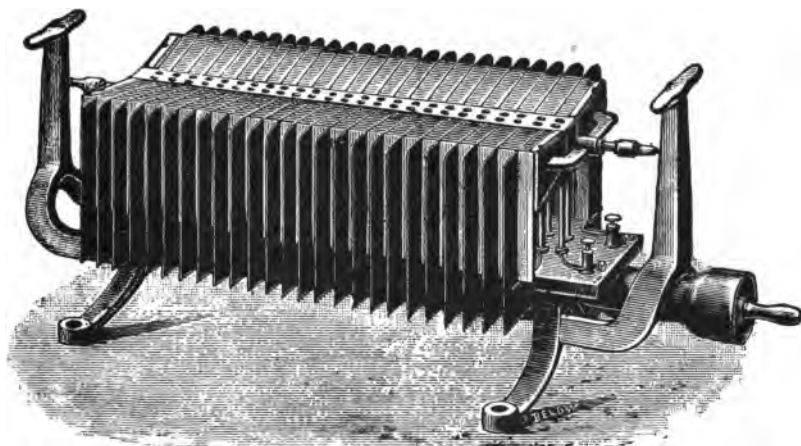
LITERATURE.—*Z. f. a. Ch.*, 14, 350; 17, 205; *Ding. p. Jr.*, 224, 267; *Z. f. a. Ch.*, 18, 457; 25, 539; *Z. f. ang. Ch.* (1809), Heft 18, 548.

The best source of electric energy, for electrolytic pur-

poses, is unquestionably the storage cell which gives a very constant current.

A form of this cell recently developed and deserving mention is known as the "Chloride Accumulator" (Fig. 12); it is of the Plante type. The largely increased surface of available plate for corrosion by the current is secured by casting a frame of lead around square or circular tablets of lead chloride mixed with zinc chloride, and then

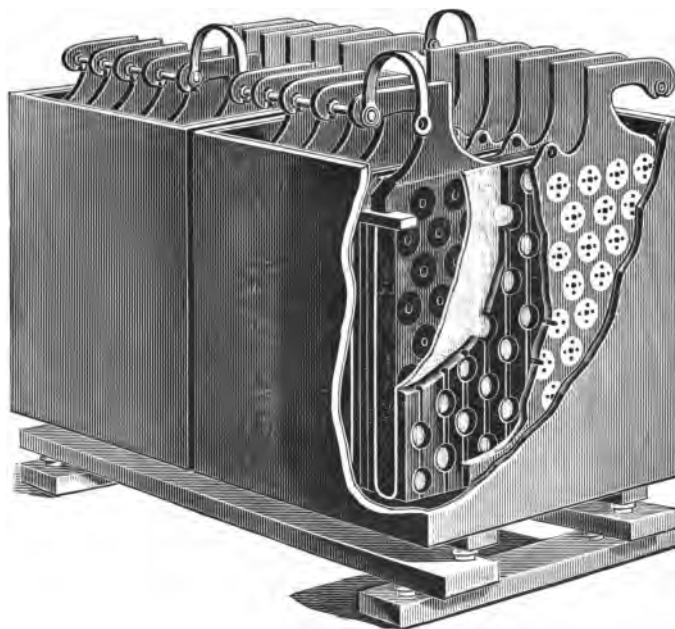
FIG. 11.



reducing these to metallic lead by means of zinc in an acid zinc chloride solution. In this way a plate is obtained which is readily "formed" by the action of the current, the oxygen rapidly converting its porous portion into peroxide. An uneven number of these peroxidized or positive plates are placed with an even number of the metallic lead or negative plates, to form a battery, the total number of plates being fixed by the capacity required. Thus, one positive plate $7\frac{3}{4}$ inches square, placed between two

negative plates of the same size, and immersed in sulphuric acid of specific gravity 1.275, forms a battery having a normal storage capacity of 50 ampere-hours. The weight of the plates in this cell is 13 pounds. The resistance of the "Chloride Accumulator" is very low. The great merit of the cell lies in its wide adaptability to the

FIG. 12.



conditions of use. It can be charged and discharged at varying rates without injury, and shows no sulphating when discharged below its normal minimum voltage. It is manufactured by the Electric Storage Co., of Philadelphia.

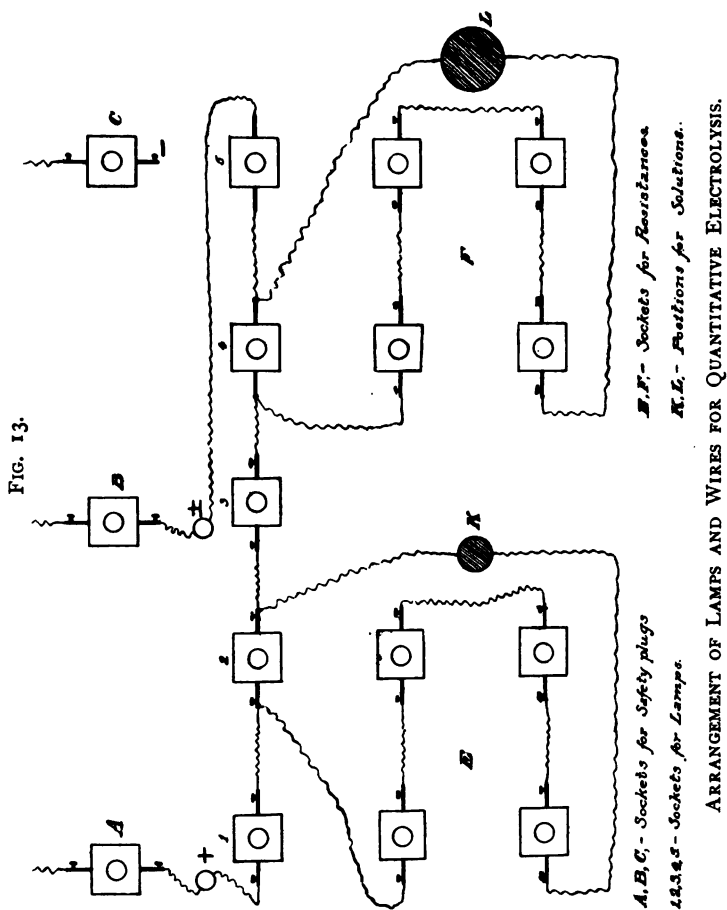
Cells of this kind can be charged from primary batteries,

or, better, by means of a dynamo or thermopile (p. 22). In any community where electric lighting is employed it is possible to have the charging done at little expense, and in factories, where there is always sufficient power, a small dynamo could easily be arranged for this purpose, so that almost any number of cells could be kept in condition for work. The iron estimations required by any establishment could be rapidly and accurately made with three cells of this type; little attention would be demanded from the chemist. While storage cells can be used in almost every description of electrolysis, there are a great many cases where economy would suggest the use of the cheaper batteries—*e. g.*, the Crowfoot. Consult the following literature upon storage batteries:—

Wied. Ann., 34 (1888), 583; Proceedings of the Royal Society, June 20, 1889; Transactions of Am. Inst. Mining Engineers (Electrical Accumulators, Salom), Feb., 1890. Elektrotechnische Zeitschrift, Jahrg. 1890; Heppé, Akkumulatoren für Elektrizität, Berlin, 1892; Z. f. ang. Ch., 1892, p. 451; Ch. Z., Jahrg. 17, 66; Die Akkumulatoren, Elbs, 2te Auflage, 1896, Leipzig; Introduction to Electrochemical Experiments, F. Oettel (translation by Smith), Philadelphia, 1897; Pfitzner, Die elektrischen Starkströme, Leipzig.

Stillwell and Austen have recently suggested the use of the electric light current for the determination of metals in the electrolytic way. That portion of their communication, in which is embodied all that is essential for those desirous of adopting this method, will be found in the following quotation: "The whole apparatus can be made from a few yards of insulated copper wire, some 16 wooden lamp sockets, and blackened lamps, say six 50-candle power, three 32-candle power, six 24-candle power, and six 16-candle power. . . . Binding screws, connections, and plugs will also be necessary in addition to those which are put in with the electric wires.

"The main wires $+$, $\pm$, $-$, are furnished with sockets A, B, C for the introduction of safety plugs, which, for the



small currents used in electrolytic work, need not exceed 6 lamp leads. The main wires terminate in binding screws, by which they are connected with the series of

sockets 1, 2, 3, 4, 5. In these lamps for reducing the main current are placed, and if only one determination or like determinations are required to be made, only this series will be necessary if ordinary currents are required. If, however, two or three different determinations, or some requiring very small currents, are to be made, side currents can be formed as around sockets 2 and 4, and the current brought to the desired size by the introduction of resistances in the series of sockets E and F. K and L will represent the proper position of the solutions to be electrolyzed by these side currents. By this arrangement three unlike determinations can be simultaneously made, one in the main circuit, and one in each of the side-series. If more determinations are required, other sets of sockets may be put up and potentials be taken over other lamps. The sockets may be placed on the wall above the desk, the wires leading down to the solutions to be electrolyzed." (Jr. An. Ch., 6, 129.) Any other arrangement can be adopted. That just described can be adjusted to the parallel system.

The current may be derived from an Edison three-wire system or from any other incandescent system.

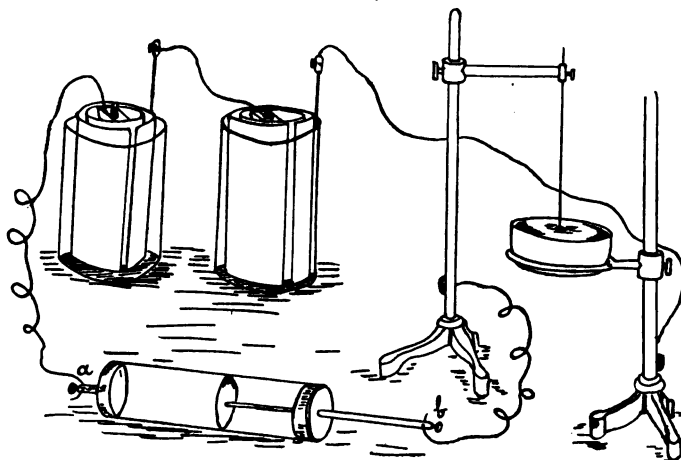
Dr. Hart, of Easton, Pa., has devised a resistance frame to be used when the electric light current is employed for electrolytic purposes. It is simpler in construction than that described in the preceding paragraph. Baker & Adamson, of Easton, manufacture this frame; particulars in regard to it can be obtained from them.

Having thus briefly described the more important current-producers, the means of regulating the current may be next considered.

4. REDUCTION OF THE CURRENT.

It is often necessary to reduce strong currents. Persons acquainted with practical physics will promptly suggest the resistance coils found in physical laboratories as suitable for this purpose. They are, on the whole, quite satisfactory, and have been thus utilized, although simpler and more convenient current-reducers have made their

FIG. 14.

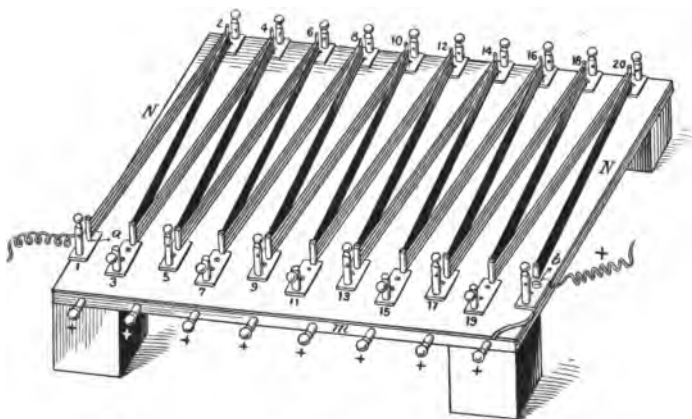


appearance in recent years. A few of these later appliances may be mentioned:—

The current may be sent through a solution (saturated) of zinc sulphate, contained in a large glass cylinder, about 22 cm. long and 8.5 cm. in diameter. In one experiment the current is passed from *a* to *b* (Fig. 14), and in the next from *b* to *a*. "The rod *b*, with one zinc pole, is pushed toward the zinc pole *a*, until the current reaches the desired strength." It is well to amalgamate the zincs

from time to time. We are indebted for this piece of apparatus to Classen, who has also described another simple rheostat (Fig. 15) (Ber., 21, 359). In this apparatus the current enters at *a*, travels the German silver resistance *N*, and returns through *b* to the battery. In the performance of electrolytic depositions the platinum vessels, serving as negative electrodes, may be connected

FIG. 15.



with any one of the binding-posts from 1 to 20. This makes it possible for the analyst to execute eight different determinations at the same time. To show the influence of this apparatus, a current from five Bunsen cells, generating 68 c.c. of oxyhydrogen gas per minute, was allowed to act upon copper solutions contained in six vessels. The current at binding-post 1 was found to be equal to 3.75 amperes; at 2, it equaled 2.617 amperes; at 3, 2.085 amperes; at 4, 1.911 amperes, etc., until at 20 it was only 0.098 of an ampere.

To better understand these figures it should be remembered that an ampere equals 10.436 c.c. of oxyhydrogen gas per minute, or it is equivalent to a current which will precipitate 19.69 mg. of metallic copper, or 67.1 mg. of metallic silver in one minute.

For a larger form of apparatus somewhat similar to that

FIG. 17.

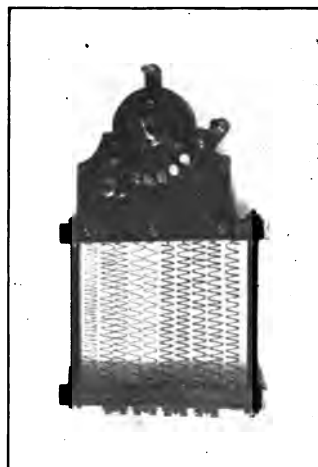


FIG. 16.

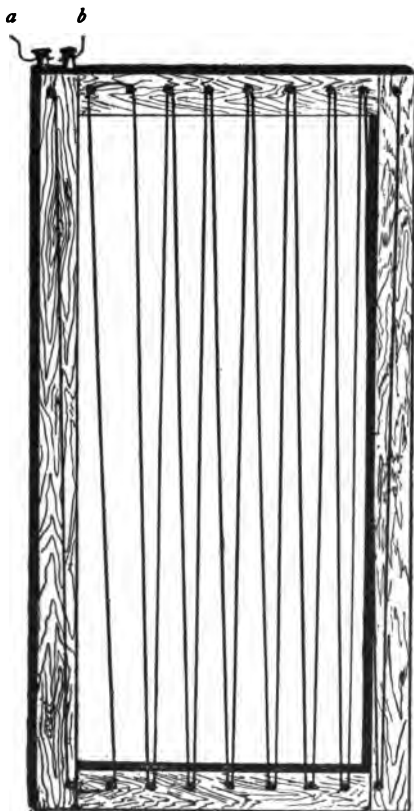


described above, see Ber., 17, 1787. Figs. 16 and 17 represent other forms of convenient and helpful rheostats.

The writer has for some time employed a much simpler current-reducer, which has the advantage of cheapness and ready construction to recommend it. It consists of a light wooden parallelogram, about six feet in length. Extending from end to end, on both sides, is a light iron wire, measuring in all about 500 feet (Fig. 18). With the

binding-posts at *a* and *b*, and a simple clamp, it is possible to throw in almost any resistance that may be required.

FIG. 18.



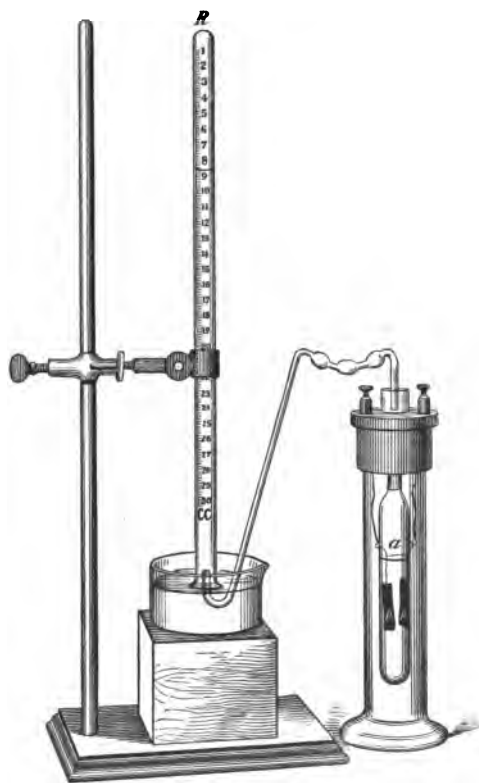
It answers all practical purposes. It can be procured from Queen & Co., Philadelphia, Pa.

LITERATURE.—V. Klobukow, Jr. f. pkt. Ch., 37, 375; 40, 121; Oettel's *Electrochemical Experiments* (Smith), P. Blakiston's Son & Co., Phila.

5. MEASURING CURRENTS, VOLTAMETER, AMPEREMETER.

In every analysis by electrolysis it is advisable that the strength of the acting current should be known. The

FIG. 19.



Bunsen voltameter (Fig. 19) may be used for this purpose. The inner tube *a*, containing sulphuric acid of sp. gr. 1.22, stands in a large cylinder of water to cool it. The liber-

ated hydrogen and oxygen are collected over water in the eudiometer tube R; p and p' are platinum electrodes. In all accurate experiments the volume of gas should always be reduced to 0° and 760 mm. pressure. Voltameters of this description are only in rare cases adapted for current measurement by introduction into the circuit. To read them the current must generally be interrupted, and they augment the resistance of the circuit to a marked degree, hence many chemists substitute a galvanometer (tangent or sine) for the voltameter. The deflection of the needle by the current measures the strength of the latter. "In order to express in terms of chemical action the deflection of the needle, it is placed in the same current with a voltameter, and the deviation of the needle is observed, as well as the volume of electrolytic gas (reduced to 0° and 760 mm. pressure) which is produced in a minute. Placing the volume equal to v , the quotient $\frac{v}{\tan. a}$ gives the standard value for the galvanometer. If this standard value is denoted by R , the strength, I , of a current which produces the deviation a is $I = R \tan. a$."

The writer has found the amperemeter of Kohlrausch (Fig. 20) very satisfactory, especially in cases where strong currents are employed. In this instrument the current travels through an insulated wire surrounding a bar of soft iron. The latter, in its magnetized state, attracts a needle or indicator and causes it to move over a vertical, graduated scale (in amperes), and its deflection gives at once the strength of the current in amperes. The Weston milli-amperemeters and ammeters will also prove most valuable in this connection.

In electrolytic work of any kind it is advisable that the apparatus intended to measure the current strength should be in the circuit during the entire decomposition,

for it is only in this way that we can expect to effect separations without encountering unpleasant difficulties. It is necessary to know just what energy is required, and then to so regulate the current that the same is approximately maintained throughout the entire determination.

FIG. 20.



When metals were first determined electrolytically no attention was given to certain very important factors. "Strong" and "feeble" currents, or currents from a two-cell bichromate battery, or five large Bunsen cells, etc., were indicated. Measuring instruments were not often used. Rarely was anything said of the size of the cathode

upon which the metal was deposited, or of the forms of the anode, the degree of dilution of the solution, and similar facts. Confusion naturally arose and contradictory statements of one kind and another were numerous. But in this, as in all other questions where there was a real desire to arrive at the truth, honest experiment soon pointed the way in which changes were necessary and also demonstrated the conditions to be observed in order that satisfactory results might be obtained. Probably then, as at present, the metal depositions were mainly made in platinum dishes, or upon cylinders or cones. These receptacles, as well as the various anode forms, will receive thorough consideration later. It is the purpose of the writer at this point to merely emphasize the most essential features in an electrolytic determination or separation. Hence note:—

1. The *current density*. To this end the inner surface of the platinum dish in which the electrolysis is made should be known in cm^2 ; its contents, too, should be given in cm^3 for various heights. $N.D_{100}$ is the *normal density* of the current; this is equivalent to the current strength for 100 cm^2 of the electrode surface. The density (D) therefore is dependent upon the current strength, as well as upon the surface (E) of the electrode upon which the metallic deposit is precipitated, *i. e.*, $D = \frac{C}{E}$.

When the surface upon which the metal is deposited equals E , the corresponding current strength can be deduced from the formula $C = (N.D_{100}) \cdot \frac{E}{100}$. See, further, Miller and Kiliani, *Lehrbuch der analyt. Chemie*, 4th ed., pp. 17–24.

2. The *potential across the poles*,—the pole pressure,—which is best determined by means of a Weston voltmeter (p. 59). This is a very important factor. A number of

interesting separations have been made by carefully regulating the pressure—voltage. See *Z. f. ph. Ch.*, 12, 97.

3. The form of the anode—whether a flat spiral, a disc of platinum, or a smaller perforated dish, suspended in the electrolyte—should also be observed, as well as its distance from the cathode.

4. The total dilution of the electrolyte and its temperature are items of value.

5. The ammeter and voltmeter should always be in the circuit.

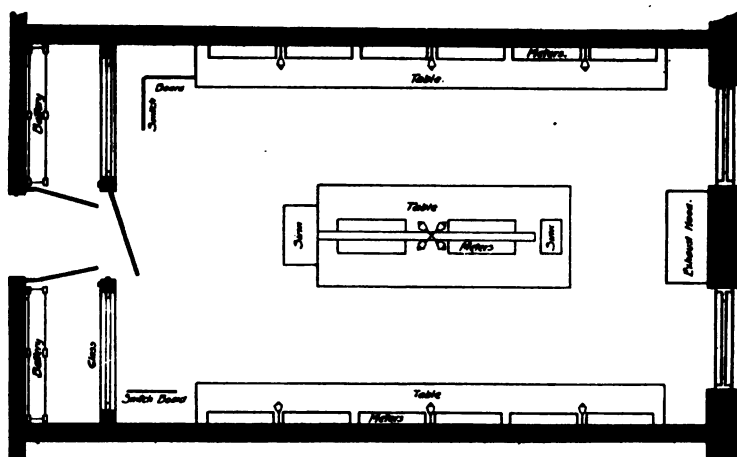
Under the individual metals these points will be taken up more fully. By strict adherence, however, to these cardinal features no one need fear the outcome. It will in every way be satisfactory.

As the importance of electro-chemical analysis has become evident, there has been marked improvement in the various forms of apparatus used in this work, and increased facilities for the same are noticed on all sides. In every well-appointed laboratory provision is made for this field of study, and in certain institutions rooms are set aside and especially equipped to carry out such work. Here at the University of Pennsylvania, where electrolytic determinations were made as early as 1878, with no special appointments and with the most primitive forms of apparatus, there has been a gradual evolution and development in apparatus and facilities according to demands and with increased knowledge, until recently an installation has been made for this as well as for other lines of work in electro-chemistry, which is characterized by great completeness and such simplicity that a brief sketch of the plant may be well introduced here.

AN ELECTRO-CHEMICAL LABORATORY.

This laboratory will accommodate at least sixteen students, working continuously. The room available for this purpose (Fig. 21) is fifteen feet by twenty-six feet, thus affording each individual three feet by twenty inches of table space.

FIG. 21.



ELECTRO-CHEMICAL LABORATORY.

Storage cells supply the energy. Those in use have a capacity of 120 ampere-hours, with a normal discharge rate of 15 amperes and a maximum rate of 30 amperes. The compartments, indicated at the end of the room, contain two groups of twenty-four cells each. They supply their respective sides of the room. They are supported on racks of four shelves each, six cells per shelf. Each shelf is thoroughly paraffined and a half-inch layer of ground

quartz is placed around the jars. Fig. 22 shows one of these compartments with the lead wires and cut-outs for each cell.

The switchboards are three in number, two of them each

FIG. 22.



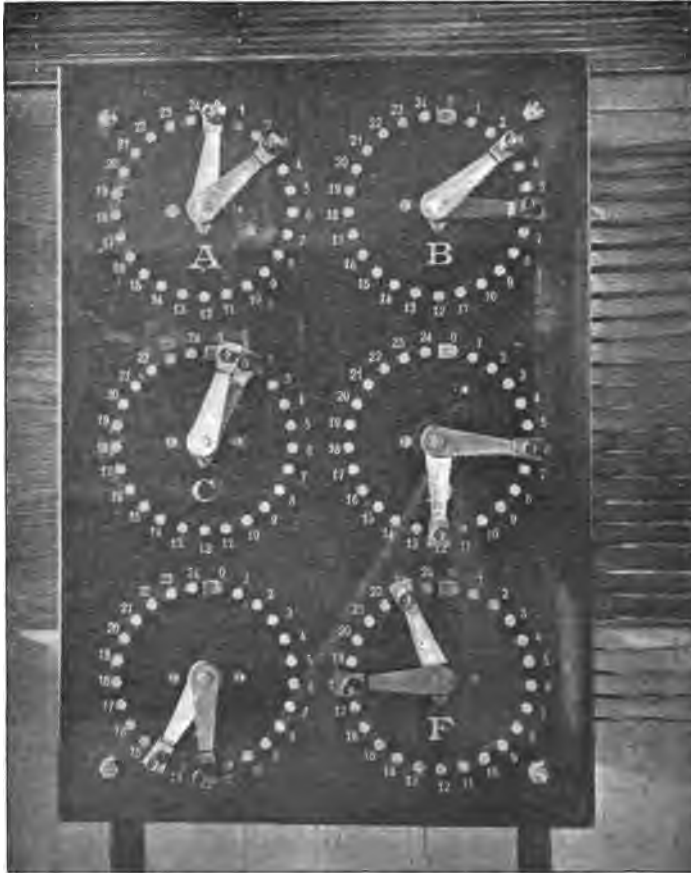
BATTERY ROOM.

controlling the six places on their respective sides of the room, and the third controlling the four places in the centre. The face of one of these boards is shown in Fig. 23, the letters on the face referring to the working tables controlled.

The switchboard on the east side of the room consists of

a slab of enameled slate twenty-four by thirty-four inches, one inch thick, and contains, for each of the six outlets to

FIG. 23.



DISTRIBUTING BOARD.

be controlled, one circle of twenty-five contact pieces, and has two spring levers, insulated from each other and mov-

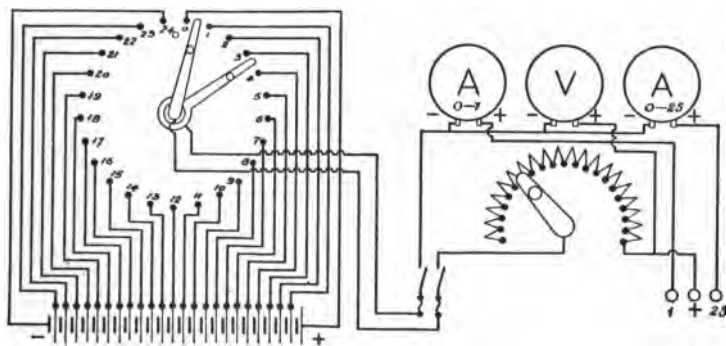
ing about a common centre, sweeping over them. The contact blocks are numbered consecutively from 0 to 24 and a stop is provided to prevent the levers from sweeping past the zero. Cell No. 1 is connected between blocks numbered 0 and 1 in each of the six circles, cell No. 2 between blocks numbered 1 and 2, and so on for the remainder of the twenty-four cells in that group, so that all blocks similarly numbered on the one board are connected together, and but a single wire leads from the six similarly numbered blocks to the junction between two cells. In this lead is provided the usual fuse. The circles are lettered A, B, C, etc., consecutively, corresponding with the letters at the outlets to be controlled.

Should the operator at the outlet E, for instance, need two cells, he goes to this board, and finding that the cells from the twelfth cell forward are not being used in any of the circles, he places one of the levers on contact block No. 12 and the other one on No. 14. There is thus very little chance of doing anything wrong, or for persons to interfere with one another, because there is no necessity to use the same cells, and at a glance one can observe which cells are in use. Fig. 24 shows the electrical connections from one of these distributing boards to the cells and outlets on the working tables. The levers themselves are too narrow at their outer ends to reach across from one block to another, to prevent short-circuiting the cells, so they are provided with fibre extensions on each side to prevent their falling between the blocks, and also to prevent their making contact with each other.

The switchboard on the west wall is exactly similar to the one just described. It contains the circles G, H, I, K, L, and M, while the third one, which controls the four outlets on the centre table, is only twenty-four inches

square, but has twenty-six contact blocks in each circle. They are numbered 0, 24, 25, 26, and so on to 48. Between the two blocks numbered 0 and 24 are connected the cells of the group on the east side of the room; between the blocks 24 and 25 is connected cell No. 1 of the west side of the room, while cell No. 2 is connected between blocks numbered 25 and 26. This arrangement connects the two groups of cells in series, and permits the use of from one to forty-eight cells at the centre table when

FIG. 24.



CONNECTIONS TO WORKING TABLE.

necessity requires. It will, perhaps, have been noticed that there is no provision made for connecting cells in parallel, and this is not necessary, as the maximum discharge rate of the cells exceeds the greatest estimated current needed by one operator.

All brass parts on the back of the board, as well as the bared ends of the wires, are thoroughly coated with P. and B. paint, while the brass parts on the front are heavily lacquered to prevent corrosion. The surface of the contact blocks can easily be cleaned with fine sandpaper.

The measuring instruments, after some deliberation, were chosen of the switchboard type. While this necessitated procuring at least one-third more instruments, yet the initial cost was considerably lower than if portable instruments had been provided, and experience with portable instruments has shown that a greater accuracy will be attained with switchboard instruments of a good form, if not immediately, yet surely after the first six months of use.

Each outlet is provided with a fused switch, a voltmeter, two ammeters, a rheostat, and a terminal board. They are connected as shown in Fig. 24. The positive lead after passing through the variable resistance runs directly to the positive binding-post. The wire coming from the negative binding-post runs to the low-reading ammeter and thence to the negative side of the switch, while the negative post marked 25 is connected to the same switch terminal, but through the ammeter of large capacity. The anode of the electrolytic cell is therefore always connected to the middle binding-post and the cathode either to post 1 or 25, depending upon the strength of current it is intended to pass through the cell. The voltmeter, being connected as shown, measures the potential differences at the terminals of the cell, except for the addition of the small fall of potential through the ammeters.

The voltmeters on the side of the room have scales ranging from 0 to 50, and divided to 1-2 volts. Those on the centre table range from 0 to 120.

The ammeters ranging from 0 to 1 ampere are divided to 1-100, and those reading from 0 to 25 are divided to 1-5 amperes. The three instruments are mounted side by side on an oak backboard extending the whole length of

the room and are covered by an air-tight case with a glass front, as shown in Fig. 25. The cases have neither doors nor a back, but are simply screwed against a backboard with a heavy felt gasket, making the joint. The wires

FIG. 25.



WORKING TABLE.

come out through hard rubber tubes sealed at their outer ends by insulating tape.

The rheostats are of the enameled type, chosen because of their being impervious to fumes. They have a total resistance of 172 ohms, divided into 51 steps in such a way that their resistances form a geometrical progression, the first step, and the sum of all the steps, being chosen in

accordance with data of the resistances of the baths determined for the work done under an earlier system.

The wires, both those in the battery rooms and those in the laboratory proper, are covered with rubber, and those in the laboratory are further encased in oak moulding, but this rather for the sake of appearance than for protection. The whole installation, as well as the other fittings of the room, has a very neat and finished appearance. (Science, 13, 697 (1901).)

Before taking up the description of the details to be observed in the electrolytic precipitation of individual metals, it may not be uninteresting to briefly trace the history of the introduction of the electric current into chemical analysis.

6. HISTORICAL.

Although the early years of last century show considerable activity in electrical studies, the efforts were mainly directed to the solution of the physical side of electrolysis. To Gaultier de Claubry probably belongs the credit of having first (1850) applied the current to the detection of metals when in solution. His efforts were wholly directed to the isolation of metals from poisons by depositing the same upon plates of platinum. When the precipitation was considered finished the plates were removed, carefully washed, and the deposited metals brought into solution with nitric acid, and there tested for and identified by the usual course of analysis. The current was evidently very feeble, as the time recorded as necessary for the deposition varied from ten to twelve hours. Gaultier considered this method reliable in all instances, but especially recom-

mends it for the separation of copper from bread. In testing for zinc he employed a strip of tin as anode, but states that a platinum plate will answer as well.

In Graham-Otto's *Lehrbuch der Chemie* (1857) it is stated that the oxygen developed at the positive electrode readily induces the formation of peroxides; . . . that lead and manganese peroxides are deposited, from solutions of these metals, upon the positive electrode of the battery; . . . that the point of a platinum wire, when attached to the anode of a cell, is therefore a delicate means of testing for manganese and lead. In the same text the oxidizing power of the anode is nicely shown by the following simple experiment: A piece of iron, in connection with the positive electrode of the battery, is introduced into a V-shaped glass tube containing a concentrated solution of potassium hydroxide, while a platinum wire running from a negative electrode projects into the other limb of the vessel. In a short time ferric acid appears around the anode, and is recognized by its color.

C. Despretz (1857) described the decomposition of certain salts by means of the electric current, and remarked that, while operating with solutions of the acetates of copper and lead, he expected both metals would be deposited upon the negative pole, and was much surprised to find that the lead separated as oxide upon the anode at the same time that the copper was deposited upon the cathode. The results were the same when experiments were conducted with the nitrates and pure acetates. With manganese no deposition took place upon the negative electrode, but a black oxide appeared at the opposite pole. Potassium antimonyl tartrate gave a crystalline metallic deposit of antimony at the cathode, and upon the anode a yellowish-red coating, supposed to be anhydrous

antimonic acid. Bismuth nitrate yielded a reddish-brown deposit at the positive electrode. Despretz concludes his paper by stating that although the facts were few in number, yet they were new in so far as they concerned lead, antimony, and manganese; and, furthermore, that the separation of copper from lead by the current was almost perfectly complete.

Three years later (1860) Charles L. Bloxam recommended the process of Gaultier for the detection of metals in organic mixtures, although it may not be improper to add that Smee (1851), in his work on electrometallurgy, asserts that Morton was the first person to employ the electric current for the isolation of metals from poisonous mixtures. However this may be, the fact remains that Bloxam did use the current quite extensively for this purpose, and while he claims no quantitative results for the method, the apparatus employed by him and his subsequent work in this direction deserve great credit.

To detect arsenic electrolytically Bloxam made use of a glass jar, four cubic inches in capacity, closed below by parchment, which was tightly secured by means of a thin platinum wire. In the neck of the jar was a large cork, through which passed a glass tube bent at a right angle. This tube was intended to serve as a means of escape for the gases liberated within the jar. The platinum wire from the negative electrode was also held in position by the cork. The portion of the wire within the jar was attached to a platinum plate dipping into the arsenical mixture containing dilute sulphuric acid. The jar with its contents stood in a wide beaker, filled with water, into which dipped the positive electrode of the battery. Under the influence of the current, metals like antimony, copper, mercury, and bismuth separated upon the plati-

num plate of the negative electrode, while arsine was liberated and escaped through the exit-tube into some suitable absorbing liquid. To ascertain what metal or metals had separated upon the cathode, the plate attached thereto was removed, after the interruption of the current, and treated with hot ammonium sulphide. Upon evaporating this solution an orange-colored spot remained if antimony had been previously present. If a metallic deposit continued to adhere to the foil, the latter was acted upon by nitric acid to effect the solution of the remaining metals.

J. Nicklès (1862) precipitated silver with the current obtained from a zinc-copper couple. The positive electrode consisted of a piece of graphite, taken from a lead-pencil, while a thin, bright copper wire constituted the negative electrode. The silver separated upon this. The current was very feeble, for hydrogen was not liberated at the cathode. Nicklès also suggested the reduction of large quantities of silver from the solution of its cyanide by this means. To obtain the silver he advised using a cylindrical cathode constructed from some readily fusible alloy, so that after the reduction was finished the other metals might be easily melted out and leave a silver plate. Copper, lead, bismuth, and antimony were separated electrolytically, by Nicklès, from textiles.

In 1862 A. C. and E. Becquerel resumed their electrochemical investigations, first begun some thirty years previously. Their experiments seem to have been aimed chiefly toward the reduction of metallic solutions upon a large scale, caring not for the quantitative estimation of metals, but seeking rather a rapid and satisfactory technical isolation process.

Wöhler (1868) found that when palladium was made

the positive conductor of two Bunsen cells, and placed in water acidulated with sulphuric acid, it immediately became covered with alternating, bright, steel-like colors. He regarded the coating as palladium dioxide, since it liberated chlorine when treated with hydrochloric acid, and carbon dioxide when warmed with oxalic acid. Black amorphous metal separated at the cathode. Its quantity was slight. Under similar conditions lead also yields the brown dioxide, and the same may be said of thallium. Osmium, in its ordinary porous form, at once becomes osmic acid. When caustic alkali is substituted for the acid, the liquid rapidly assumes a deep yellow color, while a thin deposit of metal appears upon the cathode. Ruthenium behaves similarly when applied in the form of powder. Osmium-iridium, a compound decomposed with difficulty under ordinary circumstances, immediately passes into solution when brought in contact with the positive electrode of a battery placed in a solution of sodium hydroxide, and imparts a yellow color to the alkaline liquid. A black deposit of metal slowly makes its appearance upon the negative pole.

The experiments thus far described are qualitative in their results. The first notice of the quantitative estimation of metals electrolytically was that of Wolcott Gibbs (1864), when he published the results he had obtained with copper and nickel. Luckow, in alluding to this work a year later (1865), says: "I take the liberty to observe that so far as the determination of copper is concerned, I estimated that metal in this manner more than twenty years ago, and as early as 1860 employed the electric current for the deposition of copper quantitatively in various analyses." It was Luckow who proposed the name *Elektro-Metall Analyse* for this new method of

quantitative analysis. According to this writer the current may be applied as follows:—

1. To dissolve metals and alloys in acids by which they would not be affected unaided by the electric current.

2. To detect metals like manganese and lead (silver, nickel, cobalt); separating them in the form of peroxides; also manganese as permanganic acid.

3. To separate various metals, *e. g.*, copper and manganese, from zinc, iron, cobalt, and nickel.

4. To deposit and estimate metals quantitatively, in acid, alkaline, and neutral solutions.

5. For various reductions, *e. g.*, silver chloride, basic bismuth chloride, and lead sulphate, in order that the metals in them may be determined. To reduce chromic acid to oxide, *e. g.*, potassium bichromate acidulated with dilute sulphuric acid.

These applications embrace nearly all that has since been accomplished by the aid of the current. In the same article to which Luckow calls attention to the facts recorded above, he describes minutely the method pursued by him in the precipitation of metals. Reference to these early experiments will show with what care and accuracy every detail was worked out. Luckow also announced "that all the lead contained in solution was deposited as peroxide upon the positive electrode, and might be determined from the increased weight of the latter." This observation was fully confirmed by Hampe, and later by W. C. May.

Wrightson (1876) called attention to the fact that if solutions of copper were electrolyzed in the presence of other metals, the latter greatly influenced the separation of the former. For example, with copper and antimony, the deposition of the copper was always incomplete when

the antimony equaled one-fourth to two-thirds the quantity of the former. Notwithstanding, a complete separation of the two metals can be effected when the quantity of the antimony is small. A somewhat similar behavior was noticed with other metals. The deposition of cadmium, zinc, cobalt, and nickel was apparently not satisfactory.

Lecoq de Boisbaudran (1877) electrolyzed the potassium hydroxide solution of the metal gallium, using six Bunsen elements with 20–30 c.c. of the concentrated liquid. The deposited metal was readily detached when the negative electrode was immersed in *cold* water and bent slightly.

The unpromising behavior of zinc solutions, observed by Wrightson, was fortunately overcome by Parodi and Mascazzini (1877), who employed a solution of the sulphate, to which was added an excess of ammonium acetate. Lead was also deposited in a compact form from an alkaline tartrate solution of this metal in the presence of an alkaline acetate.

After Luckow's experiments upon manganese, little attention appears to have been given this metal until Richè (1878) published his results. While confirming the observations of Luckow, he discovered that manganese was not only completely precipitated from the solution of its sulphate, but also from that of the nitrate, thus rendering possible an electrolytic separation of manganese from copper, nickel, cobalt, zinc, magnesium, the alkaline earth, and the alkali metals. Richè recommended that the deposited dioxide be carefully dried, converted by ignition into the protosulphate, and weighed as such. According to this chemist the one-millionth of a gram of manganese, when exposed to the action of the current

gave a distinct rose-red color, perceptible even when diluted tenfold.

In zinc depositions Richè gave preference to a solution of zinc-ammonium acetate containing free acetic acid.

Luckow was the first to mention that the current caused mercury to separate in a metallic form, from acid solutions, upon the negative electrode. F. W. Clarke (1878) used a mercuric chloride solution, feebly acidulated with sulphuric acid, for this purpose. The deposition was made in a platinum dish, using six Bunsen cells. Mercurous chloride was at first precipitated, but it was gradually reduced to the metallic form. J. B. Hannay (1873) had previously recommended precipitating this metal from solutions of mercuric sulphate, but gave no results.

Clarke, also, gave some attention to cadmium; his results, however, were not satisfactory. A few months later the writer (1878) succeeded in depositing cadmium completely and in a very compact form from solutions of its acetate. Upon this behavior Yver (1880) based his separation of cadmium from zinc. Furthermore, the writer found (1880) that the deposition of cadmium could be made from solutions of its sulphate, contrary to an earlier observation of Wrightson. At the same time copper was completely separated from cadmium by electrolyzing their solution in the presence of free nitric acid.

A very successful determination of both zinc and cadmium was published by Beilstein and Jawein in 1879. They employed for this purpose solutions of the double cyanides.

Heinrich Fresenius and Bergmann (1880) found that the electrolysis of nickel and cobalt solutions succeeded best in the presence of an excess of free ammonia and ammonium sulphate.

Their experience with silver demonstrated that the best results could be obtained with solutions containing free nitric acid, and by the employment of weak currents.

The writer (1880) showed that if uranium acetate solutions were electrolyzed the uranium was completely precipitated as a hydrated protos sesquioxide; and, further, that molybdenum could be deposited as hydrated sesquioxide from warm solutions of ammonium molybdate in the presence of free ammonia. Very promising indications were obtained with salts of tungsten, vanadium, and cerium.

In a more recent (1880) communication from Luckow, to whom we are indebted for much that is valuable in electrolysis, is given a full description of his observations in this field of analysis, from which the following condensed account is taken. While it relates more particularly to the qualitative behavior of various compounds, its importance demands careful study.

When the current is conducted through an acid solution of potassium chromate, the chromic acid is reduced to oxide; whereas, if the solution of the oxide in caustic potash be subjected to a like treatment, potassium chromate is produced. Arsenic and arsenious acid behave similarly. The same is true also of the soluble ferro- and ferri-cyanides and nitric acid. In the presence of sulphuric acid ferric and uranic oxides are reduced to lower states of oxidation. Sulphates result in the electrolysis of the alkaline sulphites, hyposulphites, and sulphides, and carbonates from the alkaline organic salts. In short, the current has a reducing action in acid solutions, and the opposite effect in those that are alkaline. In the electrolysis of solutions of hydrogen chloride, bromide, iodide, cyanide, ferro- and ferri-cyanide and sulphide, the hydro-

gen separates at the electro-negative pole, and the electro-negative constituents at the positive electrode. Cyanogen sustains a more thorough decomposition, the final products being carbon dioxide and ammonia. In the electrolysis of ferro- and ferri-cyanogen Prussian blue separates at the positive electrode. In dilute chloride solutions hypochlorous acid is the only product, whereas chlorine is also present in concentrated solutions. In alkaline chloride solutions chlorates are produced as soon as the liquid becomes alkaline. In the iodides and bromides iodine and bromine separate at the positive electrode, while bromates and iodates are formed when metals of the first two groups are present. Potassium cyanide is converted into potassium and ammonium carbonates. Concentrated nitric acid is reduced to nitrous acid; however, when its specific gravity equals 1.2, this does not occur, at least not when a feeble current is used. Dilute nitric acid alone, or even in the presence of sulphuric acid, is not reduced to ammonia. (See also *Z. f. anorg. Ch.*, 31, 289.) If, however, dilute nitric acid be present in a copper sulphate solution undergoing electrolysis, copper will separate upon the negative electrode and ammonium sulphate will be formed. Solutions of nitrates containing sulphuric acid behave analogously. Phosphoric acid sustains no change. Silicic acid separates as a white mass, and boric acid, in crystals uniting to arborescent groups, at the positive electrode.

In the *Ber. d. d. chem. Gesellschaft* for 1881 (Vol. 14, 1622), Classen and v. Reiss presented the first of a series of papers upon electrolytic subjects, which continued through subsequent issues of this publication. Their early work was devoted to the precipitation of metals from solutions of their double oxalates. They also

elaborated excellent methods for antimony and tin. Many very serviceable forms of apparatus, intended for electrolytic work, were devised and described by them, and it must be conceded that through the activity of the Aachen School electrolysis acquired more importance in the eyes of the chemical public than it ever before possessed. The details of the more important methods proposed by Classen and his co-laborers will receive due mention under the respective metals.

At the same time with and quite independently of Classen, Reinhardt and Ihle proposed the double oxalates for the estimation of zinc electrolytically; and in this connection it may not be improper to mention that as early as 1879, two years prior to the publication of Classen's first communication, Parodi and Mascazzini (*Gazetta chimica italiana*, Vol. 8, 178) announced that antimony and iron could be deposited completely and in compact form by electrolyzing the solutions of the sulpho-salts of the former and the chloride of the latter in the presence of acid ammonium oxalate.

In 1883 Wolcott Gibbs "gave an account of a method of electrolysis for the separation of metals from their solutions by the employment of mercury as negative electrode, the positive electrode being a plate of platinum. Under these circumstances, and with a current of moderate force, it was found possible to separate iron, cobalt, nickel, zinc, cadmium, and copper so completely from solutions of the respective sulphates that no trace of metal could be detected in the liquid. In addition it was found that phosphates of these metals dissolved in dilute sulphuric acid were easily resolved into amalgams and free acid, and the advantages of the method were pointed out in at least a certain number of cases. The author had in view both the

determination of the metal by the increase in weight of the mercury, and in particular cases of the molecule combined with the metal, either by direct titration or by known gravimetric methods." The experiments were purely qualitative, such being in the author's opinion sufficient to establish the correctness of the principle involved. "It is to be hoped that the determination quantitatively of the electro-negative atoms or molecules united with the metal will also attract attention, the method having been originally intended to serve the double purpose." This method is not applicable in the case of antimony and arsenic.

Three years later (1886) Luckow recommended a very similar procedure for the estimation of zinc.

Moore (1886) also published new data upon the estimation of iron, cobalt, nickel, manganese, etc., full notice of which will appear under these metals.

Whitfield (1886) suggested an indirect determination of the halogens electrolytically, which no doubt will prove useful.

Brand (1889) succeeded in effecting separations by utilizing solutions of the pyrophosphates of different metals.

Smith and Frankel (1889) made an extended study of the double cyanides, and found thereby a number of very convenient methods of separation heretofore unrecorded. The results of their numerous investigations in this direction are given in detail in the following pages.

Other publications relating to electrolysis are that of Warwick on metallic formates (*Z. f. anorg. Ch.*, **1**, 285), that of Frankel on the oxidation of metallic arsenides (*Ch. News*, **65**, 54), and that of Vortmann (*Ber.*, **24**, 2749) upon the electro-deposition of metals in the form of amalgams, together with a series of critical reviews of

electrolytic methods by Rüdorff in the *Z. f. ang. Ch.*, 1892.

During the past eight years the efforts in electro-chemical analysis have had for their chief purpose the perfecting of methods. The absence of reliable working conditions necessitated a careful review of earlier suggestions, with the result that while some have been abandoned, the greater number have been re-enforced and have been given a more favorable and extended use. Freudenberg (1893) revived the idea to which Kiliani first called attention, viz.: that by the application of suitable decomposition-pressures metal separations could be easily executed in the electrolytic way. This contribution, published in the *Z. f. ph. Ch.*, 12, 97, should be seriously studied by all persons interested in electro-chemical analysis. Singularly enough, the separations therein indicated had been previously made by Smith and Frankel (1889), and the statement also appears that by the use of the double cyanides the field of separations was widely extended. (See also *J. Am. Ch. S.*, 16, 93.)

The direct determination of the halogens electrolytically has been worked out by Vortmann (1895).

Other contributions have considered the availability of known electro-chemical methods to technical analysis, and many, too, have been almost wholly controversial in their character, so that they may be omitted here. The literature references to them appear in their appropriate places.

The preceding paragraphs give a brief outline of what has been accomplished in the field of analysis by electrolysis; for further information consult the following:—

LITERATURE.—*Jahrb.*, 1850, 602; *C. r.*, 45, 449; *Jr. f. pkt. Ch.*, 73, 79; *Chem. Soc. Quart. Journ.*, 13, 12; *Jahrb.*, 1862, 610; *Ann.*, 124, 131; *C. r.*,

55, 18; Ann., 146, 375; Z. f. a. Ch., 3, 334; Ding. p. Jr. (1865), 231; Z. f. a. Ch., 8, 23; 11, 1, 9; 13, 183; Am. Jr. Sc. and Ar. (3d ser.), 6, 255; Z. f. a. Ch., 15, 297; Ber., 10, 1098; Annales de Ch. et de Phy., 1878; Am. Jr. Sc. and Ar., 16, 200; Am. Phil. Soc. Pr., 1878; Z. f. a. Ch., 15, 303; Am. Ch. Jr., 2, 41; Berg-Hütt. Z., 37, 41; Z. f. a. Ch., 19, 1, 314, 324; Am. Ch. Jr., 1, 341; B. s. Ch. Paris, 34, 18; Ber., 12, 1446; 14, 1622, 2771; 17, 1611, 2467, 2931; 18, 168, 1104, 1787; 19, 323; 21, 359, 2892, 2900; Jr. f. pkt. Ch., 24, 193; Z. f. a. Ch., 18, 588; 22, 558; 25, 113; Ch. News, 28, 581; 53, 209; Ber., 25, 2492; Z. f. ph. Ch., 12, 97; Ber., 27, 2060; Z. f. Elektrochem., 2, 231, 253, 269; Z. f. a. Ch. (1893), 32, 424. And the following will be found worthy of careful study: Ann., 36, 32; 94, 1; Z. f. a. Ch., 19, 1; Berg-Hütt. Z., 42, 377; Z. f. a. Ch., 22, 485.

SPECIAL PART.

I. DETERMINATION OF THE DIFFERENT METALS.

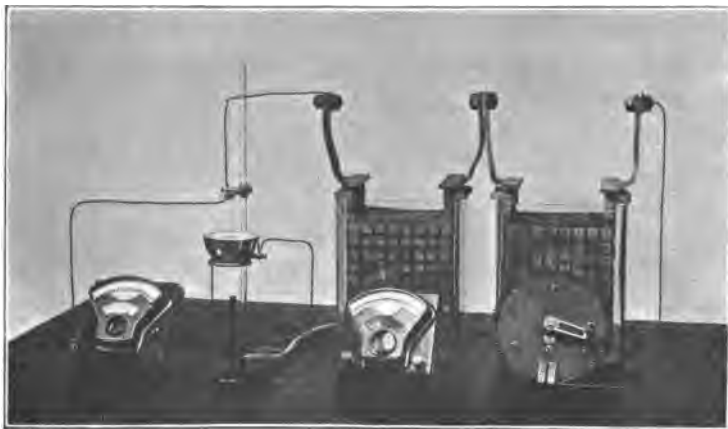
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LITERATURE.—Gibbs, Z. f. a. Ch., 3, 334; Boisbaudran, B. s. Ch. Paris, 1867, 468; Merrick, Am. Ch., 2, 136; Wrightson, Z. f. a. Ch., 15, 299; Herpin, Z. f. a. Ch., 15, 335; Moniteur Scientifique [3 ser.], 5, 41; Ohl, Z. f. a. Ch., 18, 523; Classen, Ber., 14, 1622, 1627; Classen and v. Reiss, Z. f. a. Ch., 24, 246; 25, 113; Hampe, Berg-Hütt. Z., 21, 220; Richè, Z. f. a. Ch., 21, 116; Makintosh, Am. Ch. Jr., 3, 354; Rüdorff, Ber., 21, 3050; Z. f. ang. Ch., 1892, p. 5; Luckow, Z. f. a. Ch., 8, 23; Warwick, Z. f. anorg. Ch., 1, 285; Smith, Am. Ch. Jr., 12, 329; Croasdale, Jr. An. Ch., 5, 133; Foote, Am. Ch. Jr., 6, 333; G. H. Meeker, Jr. An. Ch., 6, 267; Classen, Ber., 27, 2060; Heidenreich, Ber., 29, 1585; Regelsberger, Z. f. ang. Ch., 1891, 473; Oettel, Ch. Z., 1894, 879; Schweder, Berg-Hütt. Z., 36 (5), 11, 21; Fernberger and Smith, J. Am. Ch. S., 21, 1001; Wagner, Z. f. Elektrochem., 2, 613; Oettel, Ch. Z. (1894), 47, 879; Forster and Seidel, Z. f. anorg. Ch., 14, 106; Head, Trans. Am. Inst. Mining Engineers, 1898; Revay, Z. f. Elektrochem., 4, 313-329; Ullmann, Ch. Z., 22, 808; Hollard, C. r., 123, 1003 (1896); Kollock, J. Am. Ch. S., 21, 923.

Dissolve 19.6 grams of pure copper sulphate in water, and dilute to 1 litre. Place 50 c.c. of this solution (= 0.25 gram of metallic copper) in a *clean* platinum dish, previously weighed. Arrange the apparatus as in the accompanying sketch (Fig. 26), the voltmeter being to the left of the dish and the milliamperemeter and the rheostat to the right-hand side of the same; and having

done this, add 9–10 drops of concentrated nitric acid to the solution of the electrolyte; dilute to 125 c.c. with water; heat to 70°, and electrolyze with a current of $N.D_{100} = 0.09$ ampere and 1.9 volts. Cover the vessel with a perforated watch-crystal during the decomposition. Four to five hours will suffice for the precipitation. To ascertain when the metal has been completely precipitated, add water to the dish; this will expose a clean, platinum

FIG. 26.



surface, and if in the course of half an hour no copper appears upon it, the deposition may be considered as finished. Or a drop of the liquid may be removed and brought in contact with a drop of ammonium hydroxide or hydrogen sulphide, when, if a blue coloration or black precipitate is not produced, the deposition can be considered ended.

As the precipitation has been made in an acid solution the current should not be interrupted until the acid liquid

has been removed, for in many cases the brief period during which the acid can act upon the metal will be sufficient to cause some of the latter to pass into solution. To obviate this, siphon off the acid liquid. As the acidulated water is conveyed away by the siphon, pour distilled water into the dish. Empty the platinum dish twice in this way; the current can then be interrupted without loss of copper. Finally, disconnect the dish, wash the deposit with hot water and then with alcohol. Dry the precipitated copper at a temperature not exceeding 100° C.; an air-bath, an asbestos plate, or warm iron plate will answer for this purpose. Do not weigh the dish until it is perfectly cold, and has attained the temperature of the balance-room.

In heating the dish containing the electrolyte, do not apply a direct lamp flame; attach a circular piece of thin sheet-asbestos to the lower side of the ring, supporting the platinum dish, and under it place an ordinary Bunsen burner, or one reduced in size. Water-baths are not needed for heating purposes.

Rüdorff suggests the addition of ten drops of a saturated sodium acetate solution to the acid liquid from which the copper has been precipitated before interrupting the current. The acetic acid, which is liberated, will not immediately attack the copper, which can be at once washed and treated as just described.

Copper is very readily precipitated from solutions containing free nitric or sulphuric acid. Hydrochloric acid never should be used.

A platinum dish, 50 mm. in diameter and 20 mm. in depth, may be substituted for the spiral anode. There are openings in the dish to facilitate circulation and accelerate the precipitation of the metal.

The deposition of the copper can also be made in a platinum crucible, or upon the exterior surface of the same. This is sometimes convenient. Place the liquid undergoing electrolysis in a beaker glass (capacity 100–250 c.c.), and suspend the crucible in it (Fig. 27), supporting it there by a tight-fitting cork, through which passes a stout copper wire, *w*, in connection with the negative electrode of a battery. The positive electrode is a plati-

FIG. 27.

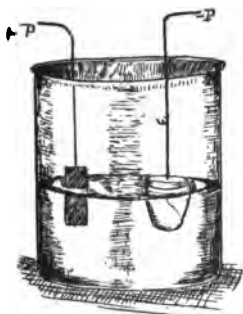
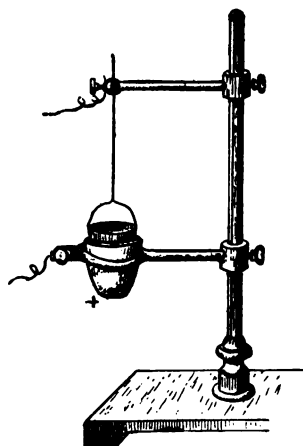


FIG. 28.



num plate projecting into the liquid. The end of the decomposition may be learned by pressing down upon *w*, or by adding water to the solution in the beaker. No further appearance of copper on the newly exposed platinum indicates the end of the precipitation. Raise the crucible from the liquid, wash the copper with water, then detach the vessel carefully from the cork, and dry as already directed.

If the current be permitted to act too long in the presence of sulphuric acid, copper sulphide may be produced. Black spots on the surface of the copper deposit indicate this.

Instead of using either of the suggestions first offered, substitute the apparatus of Richè (Fig. 28) if convenient. This consists in suspending a crucible within a crucible. The sides of the inner vessel are perforated so that the liquid will maintain uniform concentration. It is practically the same as the device just described above.

Engels recommends the addition of urea or hydroxylamine sulphate to the copper sulphate solution, as it seems to favor the deposition of the metal. He, therefore, proceeds as follows: Add 10–15 c.c. of concentrated sulphuric acid and 1.5 grams of hydroxylamine sulphate, or 1 gram of urea, to the salt solution, dilute to 150 c.c. with water, heat to 70° , and electrolyze with a current of $N.D_{100} = 0.8\text{--}1.0$ ampere and 2.7–3.1 volts. The metal will be precipitated in one and one-half hours.

Copper can also be precipitated from the solution of ammonium-copper oxalate. To this end the copper solution (sulphate or chloride) is treated with an excess of a saturated solution of ammonium oxalate diluted to 120 c.c. with water; heated to 60° and electrolyzed with $N.D_{100} = 0.35\text{--}1.0$ ampere and 2.5 to 3.2 volts. As the metal begins to separate, and the original deep blue color of the liquid disappears, add 20–30 c.c. of a cold saturated solution of oxalic acid. This should be added gradually from a burette. Avoid the precipitation of insoluble copper oxalate. When the decomposition is finished, decant the solution, and wash the deposit of copper repeatedly with water and then with alcohol. Dry as previously directed. The precipitation is generally complete after three hours.

Use ferrocyanide of potassium to learn whether all the metal has been precipitated.

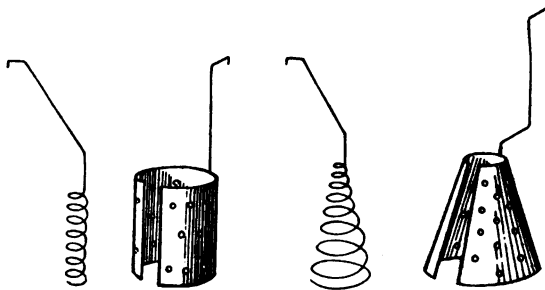
E. Wagner recommends the following procedure in the precipitation of copper from an oxalate solution: Pour the copper solution into the ammonium oxalate solution (4 grams of ammonium oxalate in 60 grams of water for 1 gram of copper sulphate); at the beginning electrolyze with a current of 0.05 ampere for one-half hour, then introduce 5 c.c. of a cold saturated solution of oxalic acid, and at the expiration of five minutes increase the current to 0.3 ampere. The temperature of the electrolyte should equal 60°. In the following eighty minutes, during four intervals, 5 c.c. of oxalic acid are added at each period and the maximum current of 0.4 ampere is applied. Two hours after the close of the circuit neither ammonia nor potassium ferrocyanide will show the copper reaction with the solution. The liquid should be siphoned off without the interruption of the current. The deposit of copper should be washed and dried as previously indicated.

Copper can also be determined quite accurately in solutions of the phosphate in the presence of free phosphoric acid, or in a formate solution containing free formic acid.

The following example is given to show the applicability of an acid phosphate solution for this particular purpose: To a solution of copper sulphate (= 0.1239 gram of copper) were added 20 c.c. of a solution of disodium hydrogen phosphate (sp. gr. 1.0358) and 5 c.c. of phosphoric acid (sp. gr. 1.347). It was then diluted to 225 c.c. with water, heated to 65°, and electrolyzed with a current of $N.D_{100} = 0.035-0.068$ ampere and 2.2–2.6 volts. The precipitation was completed in six hours. The deposit of copper weighed 0.1238 gram. It was washed and dried as previously directed, p. 60.

Rüdorff obtained excellent results with the following conditions: 0.1–0.3 gram of metallic copper in 150 c.c. of water, to which were added 2–3 grams of potassium or ammonium nitrate and 20 c.c. of ammonium hydroxide (0.91 sp. gr.). Electrolyze at the ordinary temperature with a current of $N.D_{100} = 1$ ampere and 3.3–3.6 volts. It is claimed that by observing the preceding conditions copper can be fully precipitated in the presence of chlorides. An excess of acetic acid should be added to the solution before the current is interrupted.

FIG. 29.

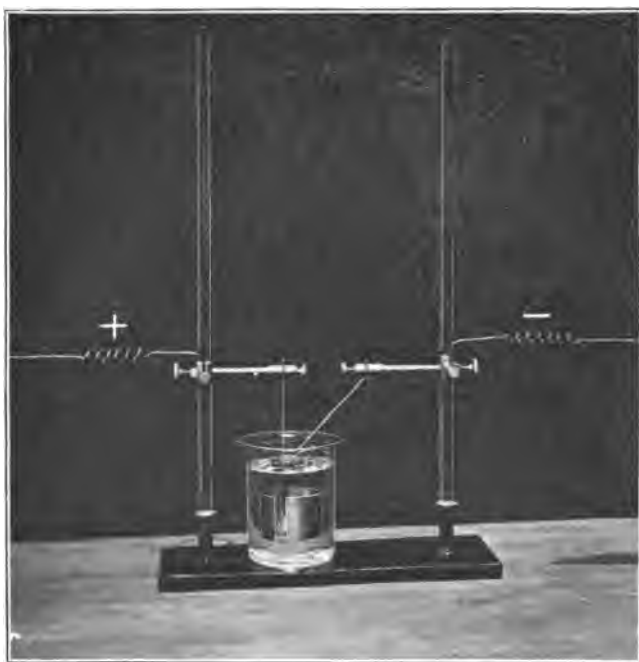


Oettel remarks on the precipitation of copper from ammoniacal solutions that the metal can be quantitatively deposited from a slightly ammoniacal liquid, containing ammonium nitrate, with a current density of 0.07–0.27 ampere per square decimetre. When ammonium nitrate is absent and the quantity of ammonia is large, the metal deposits become spongy. He found the most satisfactory concentration to be 0.8 gram of copper for 100 c.c. of liquid when using a wire-form anode with a cylinder or cone as cathode (Fig. 29). Chlorine, zinc, arsenic, and small amounts of antimony were without deleterious

effect. In the presence of lead, bismuth, mercury, cadmium, and nickel the results were high.

Moore advises dissolving the recently precipitated copper sulphide, obtained in the ordinary course of analysis, in potassium cyanide; and, after the addition of an excess

FIG. 30.



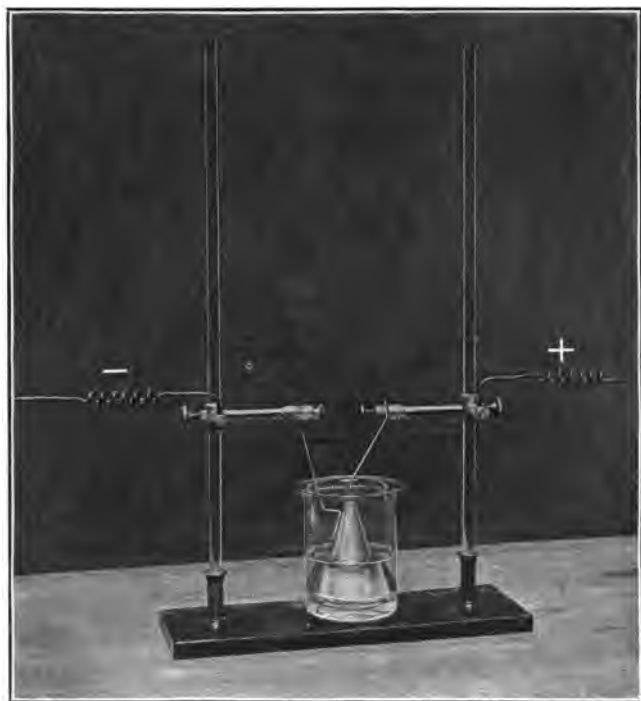
of ammonium carbonate, electrolyzes the warm (70°) solution.

In this laboratory it was observed that the electrolysis can be best and most satisfactorily executed by dissolving the sulphide in as small a volume of potassium cyanide as possible, diluting to 150 c.c. with water, heating to 65° ,

and electrolyzing with $N.D_{100} = 0.15-0.8$ ampere and 3-4.5 volts. The metal will be fully precipitated in from two to three hours.

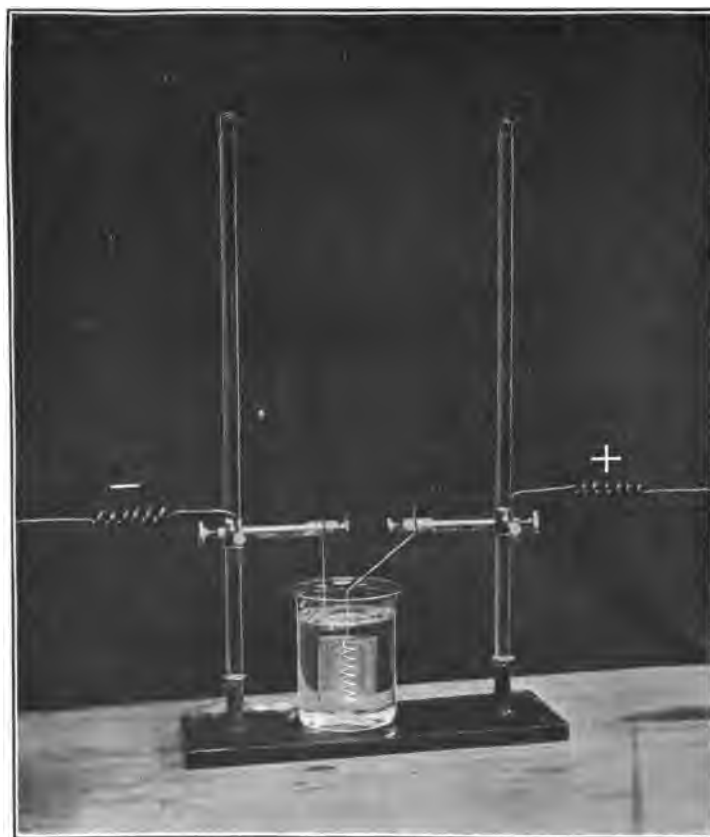
In the analysis of commercial copper Luckow employed

FIG. 31.



the apparatus pictured in Fig. 30. The beaker contains the electrolyte, and the metal is precipitated upon the cylinder of platinum. It is a very satisfactory device for almost any kind of electrolytic work. Either one of the arrangements pictured in Figs. 31 and 32 will

FIG. 32.



answer for the same purpose. The platinum gauze cathode in Fig. 32 is much favored by analysts. An anode of similar material and form can be used to advantage. To calculate the approximate surface of a cylindrical gauze cathode use the formula

$$S = \pi d 2\sqrt{n l b}$$

in which d is the diameter of the wire, n the number of meshes per square centimetre, l the length and b the width of the strip of gauze used (height of the cylinder). (Winkler, Ber., 32, 2192.)

CADMIUM.

LITERATURE.—Ber., 11, 2048; Smith, Am. Phil. Soc. Pr., 1878; Clarke, Z. f. a. Ch., 18, 104; Beilstein and Jawein, Ber., 12, 759; Smith, Am. Ch. Jr., 2, 42; Luckow, Z. f. a. Ch., 19, 16; Wrightson, Z. f. a. Ch., 15, 303; Classen and v. Reiss, Ber., 14, 1628; Warwick, Z. f. anorg. Ch., 1, 258; Moore, Ch. News, 53, 209; Smith, Am. Ch. Jr., 12, 329; Vortmann, Ber., 24, 2749; Rüdorff, Z. f. ang. Ch., Jahrg. 1892; Classen, Ber., 27, 2060; Heidenreich, Ber., 29, 1586; Wallace and Smith, J. Am. Ch. S., 19, 870; *ibid.*, 20, 279; Balachowsky, C. r., 131, 384; Miller and Page, Z. f. anorg. Ch., 28, 233; Kollock, J. Am. Ch. S., 21, 911; Avery and Dales, J. Am. Ch. S., 19, 380.

Cadmium can be determined electrolytically as readily as copper. Prepare a solution of the chloride or sulphate of definite strength. Remove 50 c.c. to a suitable, weighed platinum vessel. Add one gram of pure potassium cyanide; dilute with water to 125 c.c., heat to 60°, and electrolyze with $N.D_{100} = 0.06$ ampere and 3.2 volts. The metal will be completely deposited in five hours, or the decomposition may be begun in the evening and by morning the metal will be fully precipitated. To ascertain whether the precipitation is complete, raise the

level of the liquid in the platinum dish. In washing, it will not be necessary to siphon off the supernatant liquid; it can be poured off, after interruption of the current, without loss of metal from re-solution. Wash the deposit with cold and hot water; also with alcohol and ether. Dry upon a warm iron plate (temperature not exceeding $100^{\circ}\text{C}.$).

This metal can be deposited from the solution of its phosphate in phosphoric acid. The conditions that follow gave very satisfactory results; a current of $N.D_{100} = 0.06$ ampere and 3–7 volts acted upon 0.1656 gram of cadmium as sulphate, 30 c.c. of sodium phosphate (1.0358 sp. gr.), and $1\frac{1}{2}$ c.c. of phosphoric acid (sp. gr. 1.347). The total dilution equaled 100 c.c. The temperature of the solution was 50° . The precipitated cadmium weighed (a) 0.1654 gram and (b) 0.1657 gram. The current for the last hour of the decomposition should be increased and the deposit be washed before breaking the current.

Cadmium may also be precipitated from a solution of its sulphate containing a small amount of free sulphuric acid (2 c.c. H_2SO_4 , sp. gr. 1.09 for 0.1 gram of cadmium). Heat to 50° and electrolyze with $N.D_{100} = 0.15$ ampere and 2.5 volts. Siphon off the acid liquid before interrupting the current. Treat the deposit as previously directed.

Cadmium can also be deposited quite readily, and in a crystalline form, from its acetate solution. An example will indicate the proper conditions for a successful determination: 0.1329 gram of cadmium oxide was dissolved in acetic acid, the solution was evaporated to dryness, and the residue dissolved in 30 c.c. of water. The liquid was then heated to 50° and electrolyzed with a current of 0.02 ampere for 37 sq. cm. of cathode surface and a pressure of

3.5 volts. The metal was completely precipitated in four hours. It was crystalline and adherent. The acid liquid should be siphoned off without interrupting the current. Good results can be obtained and the period of precipitation be reduced by adding 1 gram of ammonium acetate to the solution after the current has acted for an hour. When the precipitation is completed, detach the dish, wash the deposited metal first with warm water, then with absolute alcohol, and finally with ether. Dry upon a moderately warm plate.

Balachowsky, in precipitating cadmium, makes use of a silver-coated platinum dish. Dissolve from 1.5 to 2 grams of cadmium sulphate in 100 c.c. of water, add 5 c.c. of acetic acid for every gram of salt, heat to 60° and electrolyze with a current of 0.004 ampere per sq. cm. and 2.8 volts. Later increase the current to 0.006 ampere and 3.5 volts. The deposited metal should be treated as already described.

The same chemist also obtained very satisfactory results by adding formaldehyde, acetaldehyde, or urea to the solution of cadmium sulphate. The liquid was then heated to 60° and electrolyzed with a current of 2.5–3.3 volts and 0.003 to 0.006 ampere per sq. cm.

If desired, the metal can also be precipitated from the solution of the double oxalate of ammonium and cadmium (*see* Copper), or from a formate solution in the presence of free formic acid.

When using the oxalate solution, add to it for every 0.3 to 0.4 gram of sulphate, 10 grams of ammonium oxalate, dilute to 120 c.c. with water, heat to 75°, and electrolyze with $N.D_{100} = 0.5-1.5$ amperes and 3–3.5 volts. The time necessary for complete precipitation will be three and one-half hours.

Avery and Dales employed the formate solution. Their recommendation is: Add 6 c.c. of formic acid (sp. gr. 1.20) to the solution of cadmium sulphate, then potassium carbonate until a slight permanent precipitate is formed, which is just dissolved in formic acid, after which 1 c.c. of the same acid is introduced, the liquid diluted to 150 c.c. and electrolyzed with $N.D_{100} = 0.15-0.20$ ampere and 2.6-3.4 volts.

Vortmann has determined several metals quite satisfactorily in the form of amalgams. In applying his recommendation to cadmium, add to the solution of its salt a solution of mercuric chloride and 5 grams of ammonium oxalate. Effect the solution of the latter salt without the aid of heat. This procedure is only good when small amounts of cadmium are present; cadmium ammonium oxalate is not very soluble. The current employed for the precipitation should at the very beginning of the decomposition equal from 0.6 to 0.8 ampere. When the amalgam of mercury and cadmium commences to separate reduce the current to 0.3 ampere, but gradually increase it until at the end of the decomposition it has its initial strength. If the quantity of cadmium exceeds 0.3 gram, let the solution undergoing electrolysis be ammoniacal. To this end add tartaric acid (3 grams) and an excess of ammonia to the liquid containing the mercury and the cadmium. Dilute to 200 c.c. with water. Allow the current to act until a portion of the liquid remains clear when tested with ammonium sulphide.

In the usual course of gravimetric analysis cadmium is obtained as sulphide. To prepare it for electrolysis dissolve the same in nitric acid, and after expelling the excess of the latter, add a small amount of potassium hydroxide (sufficient to precipitate the cadmium), and follow this

with an excess of potassium cyanide (1 to 2 grams). Proceed further as already directed.

MERCURY.

LITERATURE.—Ber., 6, 270; Clarke, Am. Jr. Sc. and Ar., 16, 200; Classen and Ludwig, Ber., 19, 323; Hoskinson, Am. Ch. Jr., 8, 209; Smith and Knerr, *ibid.*, 8, 206; Smith and Frankel, Am. Ch. Jr., 11, 264; Smith, Jr. An. Ch., 5, 202; Vortmann, Ber., 24, 2749; Brandt, Z. f. a. Ch., 1891, p. 202; Rüdorff, Z. f. ang. Ch., 1892, p. 5; Eisenberg, Thesis, Heidelberg, 1895; Schmucker, J. Am. Ch. S., 15, 204; Frankel, Jr. Fr. Ins., 1891; Rising and Lenher, Berg-Hütt. Z., 55, 175; Wallace and Smith, J. Am. Ch. S., 18, 169; Fernberger and Smith, J. Am. Ch. S., 21, 1006; Kollock, J. Am. Ch. S., 21, 911.

In preparing solutions for experimental purposes, use either mercuric nitrate or chloride. To a definite portion of such a solution add 3 c.c. of concentrated nitric acid dilute to 125 c.c., heat to 70°, and electrolyze with a current of $N.D_{100} = 0.06$ ampere and 2 volts. The metal will be fully precipitated in four hours. The deposit will be drop-like in appearance. The acid liquid must be removed before the interruption of the current occurs, or sodium acetate should be added; then the liquid can be decanted without the possibility of loss from resolution of the mercury (Rüdorff).

A mercuric chloride solution, feebly acidulated with sulphuric acid (0.5 c.c. of sulphuric acid), diluted to 125 c.c., heated to 65°, and electrolyzed with a current of $N.D_{100} = 0.4-0.6$ ampere and 3.5 volts, will yield all its metal in one hour. Always wash the deposited metal with cold water. Rüdorff adds the following substances to the liquid containing the mercury salt: 0.5 gram of tartaric acid and 10 c.c. of ammonium hydroxide (sp. gr. 0.91), or 5 c.c. of nitric acid, 10 c.c. of a saturated solu-

tion of sodium pyrophosphate, and 10 c.c. of ammonium hydroxide. A current of 0.02 ampere will precipitate the mercury in a compact, adherent form.

From experiments made in this laboratory the writer prefers and would especially recommend solutions of the double cyanide of mercury and potassium for the electrolytic deposition of mercury. To the mercury salt solution add 1 gram of pure potassium cyanide for every 0.1–0.2 gram of metal, dilute with water to 100 c.c., heat to 65°, and electrolyze with a current of $N.D_{100} = 0.02-0.07$ ampere and 1.6–3.2 volts. As much as 0.25 gram of metal can be deposited in three hours. This procedure requires no further attention after it is once set in operation. The deposit is always compact, and gray in color. Use water only in washing it, for alcohol seems to detach some of the metallic film.

Classen recommends the double oxalate solution for electrolytic purposes, and to that end adds to the mercuric chloride solution from 4 to 5 grams of ammonium oxalate, dilutes with water to 120 c.c., and electrolyzes at 29–37° with a current of $N.D_{100} = 1$ ampere and 4.05–4.7 volts. The mercury comes down in a perfectly adherent form, the time depending entirely upon the pressure.

The precipitation is also very satisfactory in a phosphoric acid solution, as is seen in the following example: To a solution, containing 0.1159 gram of mercury, were added 30 c.c. of sodium phosphate (sp. gr. 1.038) and 5 c.c. of phosphoric acid (sp. gr. 1.347), after which it was diluted to 175 c.c. with water, heated to 50°, and electrolyzed for four hours with a current of $N.D_{100} = 0.04$ ampere and 1.6 volts. The deposit of mercury weighed 0.1162 gram. It was treated in the usual manner.

In general analysis mercury is frequently obtained as

sulphide. Its determination in this form requires time and exceeding care. It is, however, soluble in the fixed alkaline sulphides containing free alkali. The writer has discovered that such a solution can be electrolyzed without difficulty; the mercury is deposited from it in a very compact form. An actual analysis conducted in this laboratory will best present the proper conditions for a successful determination: 20 c.c. of a sodium sulphide solution (sp. gr. 1.19) were added to a mercuric chloride solution (= 0.1903 gram of mercury), and the whole then diluted to 125 c.c. with water. This was acted upon with a current of $N.D_{100} = 0.11$ ampere and 2.5 volts for five hours. The temperature of the solution was 70°. The weight of the precipitated mercury was 0.1902 gram. It was further treated as advised in the preceding paragraphs. It is best to use a platinum dish as the negative electrode and a platinum spiral (p. 59) for the anode. Dry the deposit on a moderately warm plate or over sulphuric acid.

Several determinations of mercury in cinnabar were made to test the general applicability of the method. Samples of the mineral, analyzed in the usual gravimetric way, showed the presence of 85.40 per cent. of metallic mercury. Portions of the same mineral were weighed out in platinum dishes and after solution in 20 to 25 c.c. of sodium sulphide of the specific gravity previously mentioned, were diluted with water to 125 c.c. and electrolyzed at 70°, with the conditions recorded in the preceding paragraph. The period of time allowed for the precipitations never exceeded three hours. The results were:—

CINNABAR, IN GRAMS.	MERCURY, IN GRAMS.	MERCURY PERCENTAGE.
0.2167	0.1850	85.37
0.2432	0.2077	85.40

The platinum dishes were covered during the electrolytic decomposition. It should be done in the determination of every metal. Its purpose here was to prevent evaporation, thereby exposing a rim of metal, which, if in part not volatilized, would yet be changed to mercury sulphide, indicated by a dark-colored film.

BISMUTH.

LITERATURE.—Lućkow, *Z. f. a. Ch.*, 19, 16; Classen and v. Reiss, *Ber.*, 14, 1622; Thomas and Smith, *Am. Ch. Jr.*, 5, 114; Moore, *Ch. News*, 53, 209; Smith and Knerr, *Am. Ch. Jr.*, 8, 206; Schucht, *Z. f. a. Ch.*, 22, 492; Eliasberg, *Ber.*, 19, 326; Brand, *Z. f. a. Ch.*, 28, 596; Vortmann, *Ber.*, 24, 2749; Rüdorff, *Z. f. ang. Ch.*, 1892, 199; Smith and Saltar, *Z. f. anorg. Ch.*, 3, 418; Smith and Moyer, *J. Am. Ch. S.*, 15, 28; *ibid.*, 15, 101; Wieland, *Ber.*, 17, 1612; Smith and Knerr, *Am. Ch. Jr.*, 8, 206; Schmucker, *Z. f. anorg. Ch.*, 5, 199; *J. Am. Ch. S.*, 15, 203; Kollock, *J. Am. Ch. S.*, 21, 925; Wimmenauer, *Z. f. anorg. Ch.*, 27, 1; Brunck, *Ber.*, 35, 1871; Balachowsky, *C. r.*, 131, 179-182.

The electrolytic determination of bismuth has received much attention. Numerous electrolytes have been suggested. Most of them have failed in that the deposits of metal, unless very small in amount, have almost invariably been dark in color and have shown a tendency to sponginess. Yet they were in nearly all cases adherent. There has been an additional objection in many of the methods to the separation of peroxide upon the anode. In short, the appearance of bismuth at both poles has been very disturbing. For these reasons many of the earlier suggestions have been abandoned, and will be omitted from the present text.

Vortmann prefers the amalgam method, in accordance with which dissolve 0.5 gram of bismuth trioxide and 2

grams of mercuric oxide in sufficient nitric acid for the purpose, dilute with water to 150 c.c., and at the ordinary temperature electrolyze with $N.D_{100} = 1$ ampere and 3.5 volts. The amalgam, when the ratio is 4Hg to 1Bi, will be silver-white in color. It should be washed without interrupting the current, then carefully dried and weighed. The method is said to be especially well adapted for the precipitation of large quantities of bismuth.

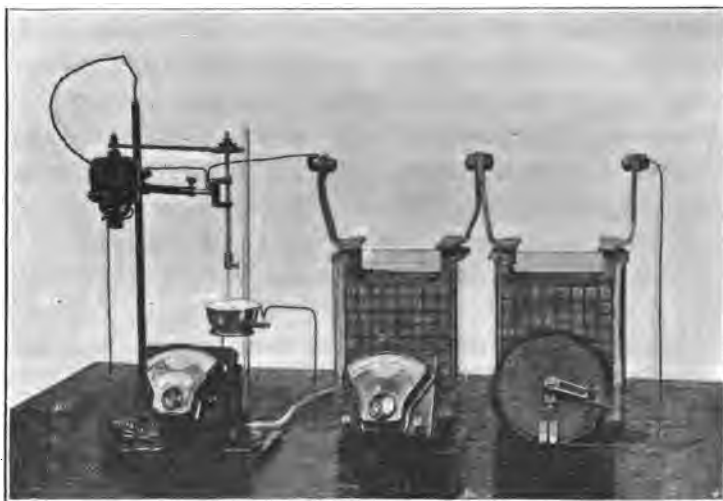
Wimmenauer has reviewed the different methods proposed from time to time, and from his experience recommends the following procedure: Dissolve 0.1–0.3 gram of bismuth nitrate in 2–4 c.c. of a glycerol solution (1 part of commercial glycerol and 2 parts of water), dilute with water to 150 c.c., and electrolyze at 50°, in a roughened dish, with a current of $N.D_{100} = 0.1$ ampere and 2 volts. The anode is rotated during the decomposition. This can be accomplished by a small electric motor, as shown in Fig. 33. The rotation is supposed to prevent the formation of peroxide, because the latter, by the movement of the anode, is immediately brought in contact with dilute nitric acid, in which it dissolves. When the anode is at rest, a protective layer of gas forms about it, and this is favorable to the deposition of peroxide. The objection may be made that this plan is involved and cannot be readily duplicated in practical work.

A. L. Kammerer, who has very recently made an exhaustive study on the electrolytic determination of bismuth in this laboratory, where he has tried every form of cathode and anode with varying electrolytes, concludes that the following conditions may be relied upon to yield satisfactory results: 0.10–0.15 gram of metal in 1 c.c. of nitric acid (sp. gr. 1.42), 2 c.c. of sulphuric acid (sp. gr. 1.84), 1 gram of potassium sulphate, 150 c.c. total dilution,

$N.D_{100} = 0.02$ ampere, $V = 1.8$. Temperature, 45° – 50° ; time, 6–7 hours.

The current should be increased the last hour to 0.15 ampere. Heat is absolutely essential in order to get a bright metallic deposit of metal. The deposit should be washed without interrupting the current, just as has been recommended with other metals when precipitated from

FIG. 33.



an acid solution. Close-fitting cover-glasses should always be used to reduce the evaporation to a minimum. The metal seemed to be deposited as well upon smooth as upon roughened surfaces.

The many successful determinations made in accordance with the directions just described indicate that the method is perhaps the best which has ever been applied in the case of this particular metal.

In determining bismuth Balachowsky keeps in view the following points: (a) A slightly acid solution; (b) the absence of large amounts of the halogens; (c) the use of a low current density (not exceeding 0.06 ampere per square decimetre); (d) a roughened dish; (e) the addition of urea or aldehyde; and offers this example: 0.06–1.7 grams of bismuth sulphate, 5–7 c.c. of nitric acid, 150 c.c. of water, 3.5–5 grams of urea; $N.D_{100} = 0.04$ – 0.06 ampere and 1–2 volts. Temperature, 60° – 70° ; time, 6–10 hours.

When it is necessary to use an alkaline citrate or citric acid solution in the precipitation of bismuth, observe the following conditions: 0.1822 gram of bismuth, 3 grams of citric acid, 125 c.c. total dilution; $N.D_{100} = 0.03$ ampere, volts = 2. Temperature, 65° ; time, 6 hours. 0.1820 gram of bismuth was found. Weigh the anode before and after the electrolysis.

LEAD.

LITERATURE.—Kiliani, *Berg-Hütt. Z.*, 1883, 253; Luckow, *Z. f. a. Ch.*, 19, 215; Richè, *Ann. de Chim. et de Phys.* [5 ser.], 13, 508; *Z. f. a. Ch.*, 21, 117; Classen, *ibid.*, 257; Hampe, *Z. f. a. Ch.*, 13, 183; May, *Am. Jr. Sc. and Ar.* [3 ser.], 6, 255; also *Z. f. a. Ch.*, 14, 347; Parodi and Mascazzini, *Ber.*, 10, 1098; *Z. f. a. Ch.*, 16, 469; 18, 588; Richè, *Z. f. a. Ch.*, 17, 219; Schucht, *Z. f. a. Ch.*, 21, 488; Tenny, *Am. Ch. Jr.*, 5, 413; Smith, *Am. Phil. Soc. Pr.*, 24, 428; Vortmann, *Ber.*, 24, 2749; Rüdorff, *Z. f. ang. Ch.*, 1892, p. 198; Warwick, *Z. f. anorg. Ch.*, 1, 258; Classen, *Ber.*, 27, 163; Kreichgauer, *Ber.*, 27, 315; *Z. f. anorg. Ch.*, 9, 89; Classen, *Ber.*, 27, 2060; Medicus, *Ber.*, 25, 2490; Neumann, *Ch. Z.* (1896), 20, 381; Hollard, *B. s. Ch. Paris*, 19, 911; Linn, *J. Am. Ch. S.*, 24, 435; Marie, *Ch. Z.*, 24, 341, 480; Nissenon and Neumann, *Ch. Z.*, 19, 1143.

The metal may be obtained by electrolyzing solutions of the double oxalate (*see* Copper and Cadmium), the acetate, the oxide in sodium hydroxide, or the phosphate

dissolved in the latter reagent or in phosphoric acid of 1.7 specific gravity. While the metal separates well from either one of these solutions, difficulty is experienced in drying the deposit, for the moist metal almost invariably suffers a partial oxidation, thus rendering the results high. The deposit can be dried, without oxidation, in an atmosphere of hydrogen, but for the inexperienced operator this procedure offers little satisfaction. It is, therefore, better to utilize the tendency of lead to separate, from acid solutions, as the dioxide. For trial purposes make up a definite volume of lead nitrate. Electrolyze several portions (= 0.1 gram lead each) in a platinum dish connected *with the anode*, using a current of $N.D_{100} = 1.5-1.7$ amperes and 2.36 to 2.41 volts. The volume of the electrolyte should be 100 c.c. and its temperature 50°-60°. In order that the lead may be precipitated wholly as dioxide upon the positive electrode and none in metallic form upon the cathode, it is necessary that the solution being analyzed should contain 20 c.c. of nitric acid of specific gravity 1.35-1.38. This quantity of acid is required when lead alone is present in solution. Chlorides must be absent. In the presence of other metals the complete deposition of the lead as dioxide occurs with even less acid. At the end of the precipitation siphon off the acid liquid and wash in the dish, then dry the deposit at 180°-190° C., and weigh. The weight multiplied by 0.866 gives the quantity of metallic lead present. The deposit can be readily dissolved in nitric acid to which oxalic acid is added, or cover it with dilute nitric acid and insert a rod of zinc or copper. Reference to the literature shows that May preferred, after drying the deposit, to carefully ignite it and finally weigh as lead oxide (PbO). This precipitation of lead as dioxide affords an excellent

method by which to separate it from other metals, *e. g.*, mercury, copper, cadmium, silver, and all those soluble in nitric acid, or those which, in a nitric acid solution, are deposited upon the cathode.

Use in these determinations a Classen dish, the inner surface of which has been roughened by having had a sand blast projected against it. The deposition of the dioxide will be much accelerated; *e. g.*, a few hours (4-5) will be sufficient for the precipitation of as much as 4 grams of dioxide upon 100 cm² surface with a current of 1.5 amperes. Wash with water and alcohol, then dry as previously directed.

The presence of arsenic in the solution lowers the lead results. When its quantity is very trifling the discrepancy may be disregarded. Selenium has a similar effect.

Lead dioxide, like manganese dioxide (p. 95), is not separated from solutions containing an excess of an alkaline sulphocyanide, and if already precipitated as dioxide, will redissolve upon the addition of the sulphocyanide.

In the analysis of lead ores Nissenson and Neumann dissolve 0.5 gram of the material in 30 c.c. of nitric acid of 1.4 specific gravity, boil, dilute with water, filter into a platinum dish, and electrolyze at 60°-70° with a current of $N.D_{100} = 1$ ampere and 2.5 volts. The dioxide is washed and dried as indicated above. One hour is sufficient for the precipitation.

The suggestion made by Vortmann that lead should be precipitated as an amalgam is not feasible, owing to certain difficulties. His method, however, will serve for the separation of the lead from a few metals.

SILVER.

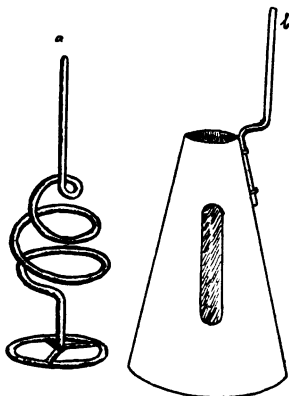
LITERATURE.—Luckow, Ding. p. Jr., 178, 43; Z. f. a. Ch., 19, 15; Fresenius and Bergmann, Z. f. a. Ch., 19, 324; Krutwig, Ber., 15, 1267; Schucht, Z. f. a. Ch., 22, 417; Kinnicutt, Am. Ch. Jr., 4, 22; Rüdorff, Z. f. ang. Ch., Jahrg. 1892, p. 5; Eisenberg, Thesis, Heidelberg, 1895; Smith, Am. Ch. Jr., 12, 335; Fulweiler and Smith, J. Am. Ch. S., 23, 583.

The experiments of Luckow showed that this metal could be deposited from solutions containing as high as eight to ten per cent. of free nitric acid. The deposit was spongy, and there was a simultaneous deposition of silver peroxide at the anode. This was, however, prevented by adding to the solution some glycerol, lactic or tartaric acid. A voluminous mass was also obtained from silver solutions, containing an excess of ammonium hydroxide or carbonate, and peroxide appeared at the same time upon the anode.

Fresenius and Bergmann, who have given the electrolysis of acid solutions of silver particular study, observed that the tendency of the metal to sponginess is most marked when the electrolyte is concentrated and acted upon by a strong current. In a dilute liquid, the current being feeble, the deposit was compact and metallic in appearance (free acid should be present). From neutral solutions, although very dilute, the metal is separated in a flocculent condition by the feeblest currents. Therefore, to obtain results that would answer for quantitative analysis, the following conditions were adopted: The total dilution of the solution was 200 c.c.; in this there were 0.03–0.04 gram of silver, and 3–6 grams of free nitric acid. The poles were separated about 1 cm. from each other, while the current at 50°–60° was $N.D_{100} = 0.04\text{--}0.05$ ampere, and at the ordinary temperature it was $N.D_{100} = 0.1\text{--}0.2$ ampere and 2 volts.

In the experiments of Fresenius and Bergmann apparatus similar to that in Fig. 34 was employed. It has some decided advantages. Both spiral (*a*) and cone (*b*) are constructed of platinum. The metallic deposition, it will be understood, occurs upon the cone, the sides of which are perforated, so that a uniform concentration of liquid is preserved throughout the decomposition. When

FIG. 34.



liquid electrolytes contain much iron, it is essential that the oxygen liberated within the cone should be equally distributed over its outer surface. This is made possible through openings. The shape of the cone also prevents loss from the bursting of the bubbles arising from the platinum spiral in connection with the anode.

Krutwig advises adding a large excess of ammonium sulphate to the silver solution, previously made alkaline with ammonium hydroxide, and employs a current of $N.D_{100} = 0.02-0.05$ ampere and 2.5 volts. In this way, 0.1 gram of silver may be precipitated in two hours.

The writer's experience has chiefly been with solutions of silver containing an excess of a pure alkaline cyanide. With these peroxide separation does not occur, and a very weak current will precipitate 0.15–0.20 gram of metal in ten hours from a cold solution. If the liquid be heated to 65° C., during the decomposition, as much as 0.2–0.3 gram of metal may be precipitated in three and one-half hours. The current density for this precipitation should be $N.D_{100} = 0.07$ ampere. Several examples from a student's notebook will show how well the method works:—

	SILVER. GRAM.	DILU- TION. C.C.	POTASSIUM CYANIDE. GRAMS.	CURRENT. N.D ₁₀₀ .	VOLTS.	TEMPER- ATURE.	TIME. HOURS.	SILVER FOUND. GRAM.
1 . .	0.2133	125	2	0.03 A	2.5	65°	4	0.2132
2 . .	0.2133	125	2	0.03 A	2.5	60°	3	0.2133
3 . .	0.2133	125	4	0.04 A	2.5	60°	3	0.2131
4 . .	0.2133	125	2	0.025 A	2.7	60°	4	0.2134
5 . .	0.2133	125	2	0.025 A	2.7	60°	3	0.2135
6 . .	0.2133	125	2	0.025 A	2.7	60°	4	0.2125

In trials 1 and 2 the metal was precipitated upon a dish, while in 3 and 4 a plate cathode, and in 5 and 6 a cone was used to receive the silver, which was very adherent, and brilliant in lustre. It was washed with water, alcohol, and ether.

Chlorine, bromine, and iodine can be indirectly estimated electrolytically by first precipitating them as silver salts, then dissolving the latter in potassium cyanide, and exposing the resulting solution to the action of a current from three to four "Crowfoot" cells.

Luckow reduced silver chloride by placing it in a platinum dish, serving as the negative electrode, covering it with dilute sulphuric or acetic acid, and allowing the positive electrode to project into the solution. Four Meidin-

ger cells were strong enough to reduce 0.1 gram of silver chloride in ten minutes. The deposit, while spongy, was adherent. It was washed with water and then thoroughly dried to insure the absence of any acid. (See the reference to Kinnicutt's experiments; also, Prescott and Dunn, Jr. *An. Ch.*, 3, 373.)

ZINC.

LITERATURE.—Wrightson, *Z. f. a. Ch.*, 15, 303; Parodi and Mascazzini, *Ber.*, 10, 1098; *Z. f. a. Ch.*, 18, 587; Richè, *Z. f. a. Ch.*, 17, 216; Beilstein and Jawein, *Ber.*, 12, 446; *Z. f. a. Ch.*, 18, 588; Richè, *Z. f. a. Ch.*, 21, 119; Reinhardt and Ihle, Jr. *f. pñt. Ch. [N. F.]*, 24, 193; Clausen and v. Reiss, *Ber.*, 14, 1622; Gibbs, *Z. f. a. Ch.*, 22, 558; Luckow, *Z. f. a. Ch.*, 25, 113; Brand, *Z. f. a. Ch.*, 28, 581; Warwick, *Z. f. anorg. Ch.*, 1, 258; Vortmann, *Ber.*, 24, 2753; Rüdorff, *Z. f. ang. Ch.*, Jahrg. 1892, 197; Vortmann, *M. f. Ch.*, 14, 536; v. Malapert, *Z. f. a. Ch.*, 26, 56; Herrick, Jr. *An. Ch.*, 2, 167; Jordis, *Z. f. Elektrochem.*, 2, 138, 563, 655; Millot, *B. s. Ch. Paris*, 37, 339; v. Foregger, *Dissertation*, Bern, 1896; Riderer, *J. Am. Ch. S.*, 21, 789; Nicholson and Avery, *J. Am. Ch. S.*, 18, 659; Paweck, *Berg-Hütt. Z.*, 46, 570-573.

Much has been written upon the electrolytic estimation of zinc. The personal experience of the writer inclines him to give preference to the method suggested by Parodi and Mascazzini. They recommended that the metal be present in solution as sulphate; its quantity may vary from 0.1-0.25 gram. To it add 4 c.c. of a solution of ammonium acetate, 20 c.c. of citric acid, and dilute to 200 c.c. with water. The electrodes are then introduced into the liquid, their distance apart being not more than a few millimetres. The precipitation can be made in a beaker glass, using a weighed platinum cone (Fig. 34) as the cathode. The current for this purpose should be 0.5 ampere and 5.9-6.3 volts. At 50°-60°, with a current of

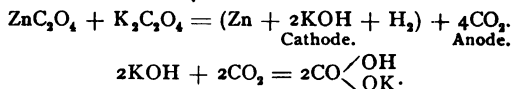
0.5 ampere, the pressure will be 4.8–5.2 volts and the deposit of metal will be most satisfactory. When the precipitation of metal has ended, which may be ascertained by removing a small quantity of the liquid with a capillary tube and bringing it in contact with a drop of a solution of potassium ferrocyanide, remove the bulk of the liquid with a siphon. Wash the deposit with water and alcohol. There is no danger of oxidation during the drying process. It will be discovered on dissolving the precipitated zinc that the platinum is covered with a black powdery layer, insoluble even in hot hydrochloric or hot nitric acid. This is platinum black (Vortmann, Rüdorff). It is exceedingly difficult to remove, and to prevent its occurrence it is best to coat the platinum dish with a thin layer of copper or silver before precipitating the zinc (p. 88).

Beilstein and Jawein add sodium hydroxide to the solutions of zinc nitrate or sulphate, until a precipitate is produced, dissolve it in potassium cyanide, and dilute with water to 150 c.c. The decomposition is carried out in a rather large beaker glass, the cathode being either the platinum cone already described (p. 82), or a rather large platinum crucible suspended from a cork (p. 61), perforated by a copper wire, touching the inner surface of the crucible. If the decomposition takes place at the ordinary temperature, use a current of $N.D_{100} = 0.5$ ampere and 5.8 volts. The precipitation will be complete in from two to two and one-half hours. It may be reduced to one and one-half to one and three-quarter hours by heating the electrolyte to 60° and applying a current of the density just given and 5 volts. Wash the deposit as instructed above.

Reinhardt and Ihle have objected to nearly all the

methods which have been proposed for the electrolytic estimation of zinc. They say of the Beilstein and Jawein method that the results are fairly good, ... but a strong current is necessary, otherwise the precipitation of the zinc is slow and incomplete, ... the positive pole diminishes in weight very appreciably, ... finally, working with potassium cyanide is very unpleasant. The writer's experience has proved that a current considerably less than that which Beilstein and Jawein first recommended will throw out all the zinc in the course of a night, and further that the anode is not appreciably affected. The method suggested by Reinhardt and Ihle is, however, very excellent and deserves trial by all interested in the electrolytic estimation of zinc. Its essential features, taken from their publication, are these: Mix the solution of zinc sulphate or chloride, neutral as possible, with an excess of neutral potassium oxalate, until the precipitate, which appears at first, redissolves. Or, observing the recommendation of Classen, add 4 grams of potassium or ammonium oxalate to the solution, acidulate the latter with tartaric acid (3 : 50), dilute to 150 c.c. with water, heat to 60°, and electrolyze in copper-coated platinum dishes with $N.D_{100} = 0.5-1.5$ amperes and 3.5-3.8 volts. Two hours will be sufficient for complete precipitation.

The immediate decomposition of the zinc oxalate is into zinc and carbon dioxide (two molecules), and the potassium oxalate into carbon dioxide (two molecules) and potassium; the latter then reacts with the water, so that while an abundant liberation of hydrogen occurs at the cathode, the alkali simultaneously set free is converted into acid potassium carbonate by the carbon dioxide at the anode:—



Therefore, just as long as zinc oxalate is being decomposed, considerable evolution of gas is noticeable at the positive electrode, and when this diminishes, and occasional bubbles escape, the decomposition is complete, and the deposition of metal may be considered finished.

Free oxalic acid, or any other acid, is not injurious if there is a sufficient quantity of potassium oxalate present. Nitric acid, however, free or combined, should be avoided; it gives rise to ammonium salts, which prevent the zinc from separating in a dense form. The acid potassium carbonate produced during the decomposition offers great resistance to the current; it is, therefore, advisable to add potassium sulphate to the solution to increase its conductivity. Reinhardt and Ihle recommend the following solutions for use in decompositions like that just described: 166 grams of potassium oxalate in 1 litre of water; 250 grams of potassium sulphate in 1 litre of water, and a solution of oxalic acid saturated at 15° C.

Experiments.—(1) 40 c.c. of a solution of zinc sulphate (= 0.1812 gram of metallic zinc), to which were added 50 c.c. of potassium oxalate and 100 c.c. of potassium sulphate, were electrolyzed with a current of $\text{N.D}_{100} = 0.3$ ampere and 3.9–4.2 volts, at the ordinary temperature. After three to four hours the current was interrupted. The precipitated zinc weighed 0.1814 gram. (2) 2.1867 grams of brass (containing tin, copper, lead, and zinc) were dissolved in nitric acid and the tin determined in the usual gravimetric way. Its quantity was found to be 0.04 per cent. In the filtrate, containing nitric acid, lead and copper were determined simultaneously by electrolysis

(the copper separated upon the cathode and the lead as dioxide upon the anode):—

$$\text{Found } \left\{ \begin{array}{l} a-0.85\% \text{ Pb and } 64.60\% \text{ Cu.} \\ b-0.85\% \text{ " " } 64.62\% \text{ " "} \end{array} \right.$$

The acid liquid was siphoned off from the deposits, evaporated to dryness with sulphuric acid, neutralized with caustic potash, and then to this (100 c.c. in volume) solution were added 50 c.c. of a solution of potassium oxalate and 100 c.c. of a solution of potassium sulphate. The zinc found equaled 34.50 per cent.

When using this method employ a stout platinum wire, wound to a spiral at the one end, for the anode, and a platinum cone for the cathode (p. 82). To avoid the peculiar spots which electrolytic zinc shows upon a platinum surface, it will be best to first coat the negative electrode with copper (5 grams). In dissolving the precipitated zinc, use rather dilute nitric acid. The copper layer will be but slightly attacked, and after washing and drying will serve for further depositions. Wash the zinc deposit with water, alcohol, and ether; dry in a desiccator. Oxidation is liable to occur if an air-bath be used for the drying.

Jordis prefers lactic to oxalic acid in the electrolysis of zinc salts. To the solution containing 0.2 gram of metallic zinc he added 5 grams of ammonium lactate, 2 grams of lactic acid, and 5 grams of ammonium sulphate. The liquid was diluted to 230 c.c. and acted upon at 60° with a current of $N.D_{100} = 0.10-0.23$ ampere and 3.4-3.9 volts. The electrolyte was usually agitated (p. 77). The anode and cathode were 1.5 cm. apart. The time for complete precipitation occupied four and a quarter hours. A copper-plated platinum dish was used as cathode.

Nicholson and Avery, adopting the suggestion of Warwick, add 3 c.c. of formic acid to the zinc salt solution, then nearly neutralize with sodium carbonate, dilute to 150 c.c., and electrolyze at the ordinary temperature with a current varying from 0.5 to 1 ampere.

Millot, Kiliani, and v. Foregger use sodium zincate as electrolyte, giving the following example: To the solution of 1 gram of zinc sulphate add 2 to 4 grams of sodium hydroxide, dilute to 125 c.c. with water, heat to 50°, and electrolyze with $N.D_{100} = 0.7-1.5$ amperes and 3.9-4.5 volts. All of the metal will be deposited in two hours. The character of the deposit is improved with the increase in the quantity of sodium hydroxide.

Richè employs "a solution of the acetate with an excess of ammonium acetate, obtained by supersaturation with ammonia and acidifying with acetic acid." This method affords good results, as may be seen from the following determination: 0.4736 gram of zinc sulphate was dissolved in 200 c.c. of water, to which were added 3 grams of sodium acetate and 10 drops of ordinary acetic acid. When there is an insufficiency of acetic acid, the zinc deposit becomes spongy. Ammonium acetate may be substituted for the sodium salt. After two hours 0.1063 gram of metallic zinc was obtained, the required quantity being 0.1072 gram. The temperature should be 60° and the current $N.D_{100} = 0.5$ ampere and 4.8-5.2 volts.

Moore seems to have obtained exceedingly satisfactory results by precipitating a solution of zinc sulphate with sodic phosphate, then adding an excess of ammonium carbonate, and after dissolving the precipitate in potassium cyanide, the solution was electrolyzed at a temperature of 80°. (See method of Beilstein and Jawein.) The metal was deposited upon a silver-plated electrode. An

excellent procedure, originating with Luckow and previously noticed in the Historical section, consists in introducing 0.5 gram of metallic mercury into the dish in which it is intended to electrolyze the solution of the zinc salt. It is, of course, understood that the platinum dish and the drop of mercury are weighed together. A zinc amalgam is precipitated; it distributes itself in a beautiful adherent layer over the surface of the dish.

Paweck believes that in the amalgam method suggested by Vortmann much inconvenience is experienced in weighing out the mercuric chloride and subsequently re-calculating it into metal; further, that by frequent use the surface of the platinum cathode changes to spongy platinum, thus giving rise to considerable loss. To avoid these disadvantages he suggests the use of amalgamated zinc or brass electrodes in gauze form. The introduction of these eliminates the addition of a mercury salt, while the gauze form favors the deposition and prevents the collection of hydrogen bubbles on the under side of the cathode, whereby a spongy zinc deposit is likely to be produced. The gauze electrodes are semi-cylindrical in shape, 6 cm. in diameter, two being attached to a brass rod at a distance of 12 mm. After they have been cleaned, they are amalgamated or coated with mercury by electrolyzing a solution containing 0.6 gram of mercuric chloride. The amalgam is washed with alcohol, ether, dried and weighed. The electrolyte contains the zinc salt, Seignette salt, and alkali. It may be electrolyzed with a current of 0.1–0.5 ampere and 2.6–3.6 volts. The deposit should be dried at 30°–40°. (See p. 60.)

Vortmann has found that zinc may be readily precipitated from its solution in the presence of an excess of sodium hydroxide and sodium tartrate. The deposit is

gray in color and adheres well to the dish. The current density ($N.D_{100}$) may vary from 0.3–0.6 ampere. To determine when the precipitation is complete, remove a few drops of the liquid and warm with ammonium sulphide.

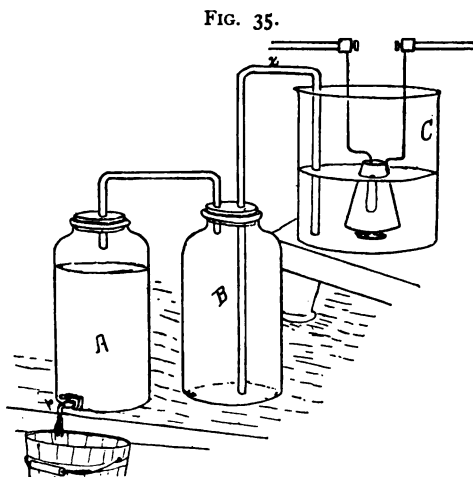
NICKEL AND COBALT.

LITERATURE.—Gibbs, *Z. f. a. Ch.*, 3, 336; *Z. f. a. Ch.*, 11, 10; 22, 558; Merrick, *Am. Ch.*, 2, 136; Wrightson, *Z. f. a. Ch.*, 15, 300, 303, 333; Schweder, *Z. f. a. Ch.*, 16, 344; Cheney and Richards, *Am. Jr. Sc. and Ar.* [3], 14, 178; Ohl, *Z. f. a. Ch.*, 18, 523; Luckow, *Z. f. a. Ch.*, 19, 16; Bergmann and Fresenius, *Z. f. a. Ch.*, 19, 314; Richè, *Z. f. a. Ch.*, 21, 116, 119; Classen and v. Reiss, *Ber.*, 14, 1622, 2771; Schucht, *Z. f. a. Ch.*, 21, 493; Kohn and Woodgate, *Jour. Soc. Chem. Industry*, 8, 256; Rüdorff, *Z. f. ang. Ch.*, Jahrg. 1892, p. 6; Brand, *Z. f. a. Ch.*, 28, 588; Le Roy, *C. r.*, 112, 722; Vortmann, *M. f. Ch.*, 14, 536; v. Foregger, *Dissertation*, 1896, Bern; Campbell and Andrews, *J. Am. Ch. S.*, 17, 125; Oettel, *Z. f. Elektrochem.*, 1, 192; Fresenius and Bergmann, *Z. f. a. Ch.*, 19, 320; Foster, *Z. f. Elektrochem.*, 6, 160; Winkler, *Z. f. anorg. Ch.*, 8, 291.

These metals are precipitated from solutions of their double cyanides, double oxalates, and sulphates mixed with alkaline acetates, tartrates, and citrates, or from ammoniacal solutions. The latter seem best adapted for nickel depositions, the presence of ammonium sulphate or sodium phosphate being favorable to the precipitation.

Fresenius and Bergmann, who have carried out a series of experiments with nickel and cobalt, give the following as satisfactory conditions: 50 c.c. nickel solution (= 0.1233 gram of nickel), 100 c.c. of ammonia (sp. gr. 0.96), 10 c.c. of ammonium sulphate (305 grams of the salt in 1 litre of water), 100 c.c. of water; separation of the electrodes $\frac{1}{2}$ – $\frac{1}{3}$ cm.; time, four hours. The current was $N.D_{100}$ = 0.5–0.7 ampere and 2.8–3.3 volts at the ordinary tem-

perature. The nickel found weighed 0.1233 gram. Apparatus suitable for the decomposition just described is represented in Fig. 35. The metal is deposited upon the weighed platinum cone in the beaker glass, C. The vessel is covered with a glass lid having suitable apertures for the positive and negative electrodes. As soon as the blue-colored liquid becomes colorless, an indication that the metal is completely precipitated, re-



move a few drops and test with a solution of potassium sulphocarbonate. If the latter causes only a faint rose-red coloration the deposition of metal may be considered complete. If the electrolysis is unnecessarily prolonged, metallic sulphide may be produced (*Lehrbuch der analyt. Chemie*, Miller and Kiliani). It is not advisable to interrupt the current or to remove the cone from the electrolyzed liquid until the latter has been replaced by water. This is effected by the vessels to the left of the figure: A is

an aspirator, filled with water; *B* is air-tight and empty; *x* is a doubly bent tube extending to the bottom of *C*. Open *p* and the liquid in *C* is gradually transferred to *B*. Add fresh water in *C*. Ammonium chloride should not be present in the solution undergoing electrolysis.

Vortmann adds tartaric or citric acid and an excess of sodium carbonate to the solution of the nickel salt, then electrolyzes with a current density of $N.D_{100} = 0.3-0.4$ ampere. The deposit may contain traces of carbon.

The statements upon nickel also apply to cobalt. An experiment, taken from the article of Fresenius and Bergmann, is here given as a guide in determining cobalt: 50 c.c. of cobalt sulphate (= 0.1286 gram of cobalt), 100 c.c. of ammonia, 10 c.c. of ammonium sulphate, 100 c.c. of water; current $N.D_{100} = 0.5-0.7$ ampere and 2.8-3.3 volts at the ordinary temperature; separation of electrodes, $\frac{1}{2}-\frac{1}{3}$ cm. Time, five hours. The deposited cobalt weighed 0.1286 gram.

Use potassium sulphocarbonate to test when the metal is fully reduced; it gives a wine-yellow coloration with even the most dilute solutions of cobalt salts.

When too little ammonia is present in the electrolyte the results are bad; too much of this reagent retards the deposition of the cobalt.

v. Foregger adds 15 to 20 grams of ammonium carbonate to the solution of 1 gram of nickel sulphate, dilutes with water to 150 c.c., heats to 60°, and electrolyzes with $N.D_{100} = 1-1.5$ amperes and 3.5-4 volts. Two hours will be required for the precipitation.

Oettel observed that nickel could be, contrary to general statements, as well precipitated from an ammoniacal chloride as from an ammoniacal sulphate solution. With a current of $N.D_{100} = 0.45$ ampere in the presence of 40

c.c. of free ammonia (sp. gr. 0.92), 10 grams of ammonium chloride and nickel chloride equivalent to 1.0456 grams of metal, total dilution 200 c.c., he succeeded in throwing out 1.0462 grams of metal in six and one-quarter hours. Nitric acid should not be present. More difficulty was experienced with cobalt. The most favorable results were obtained with a current of $N.D_{100} = 0.4-0.5$ ampere. The quantity of ammonium chloride should be at least four times that of the cobalt and the solution should contain one-fifth of its volume of free ammonia (sp. gr. 0.92). When precipitating these metals from the solutions of their double oxalates, the conditions should be: 4-5 grams of ammonium oxalate, 120 c.c. total dilution, temperature $60^{\circ}-70^{\circ}$, with $N.D_{100} = 1$ ampere and 4 volts.

The writer has electrolyzed cobalt compounds containing an excess of an alkaline acetate (*see* Zinc) with perfectly satisfactory results, and would recommend such solutions for this particular metal.

In this laboratory the following conditions are observed in precipitating nickel from a cyanide solution: Add 0.1 gram more of alkaline cyanide than is necessary for the precipitation and re-solution, 2 grams of ammonium carbonate, dilute to 150 c.c., heat to 60° , and electrolyze with $N.D_{100} = 1.5$ amperes and 6-6.5 volts. The nickel will be fully precipitated in three and one-half hours. Cobalt may be precipitated under similar conditions.

Sodium pyrophosphate precipitates a greenish-white pyrophosphate from nickel solutions, an excess of the reagent dissolves the precipitate, while the liquid becomes yellow-green in color. The latter is changed to green by ammonium carbonate, and to blue by ammonium hydroxide. When electrolyzing a nickel solution add to it 20 c.c. of a sodium pyrophosphate solution, 25 c.c. of

ammonia (0.91 sp. gr.), and 150 c.c. of water. A current of 0.5 to 0.8 ampere will be sufficient to throw out the nickel in nine hours. This method will serve equally well for the estimation of cobalt.

In determining nickel, Campbell and Andrews dissolve nickel hydrate in 30 c.c. of a 10 per cent. solution of sodium phosphate, add 30 c.c. of ammonia to the same, dilute to 125 c.c., and electrolyze with $N.D_{100} = 0.14$ ampere, the electrodes being separated 5 mm. The precipitation is complete in twelve hours.

MANGANESE.

LITERATURE.—Z. f. a. Ch., 11, 14; Richè, Ann. de Chim. et de Phys. [5th ser.], 13, 508; Luckow, Z. f. a. Ch., 19, 17; Schucht, Z. f. a. Ch., 22, 493; Classen and v. Reiss, Ber., 14, 1622; Moore, Ch. News, 53, 209; Smith and Frankel, Jr. An. Ch., 3, 385; Ch. News, 60, 262; Brand, Z. f. a. Ch., 28, 581; Rüdorff, Z. f. ang. Ch., Jahrg. 15, p. 6; Classen, Ber., 27, 2060; Engels, Z. f. Elektrochem., 2, 413; 3, 286; Groeger, Z. f. ang. Ch. (1895), 253; Kaepfel, Z. f. anorg. Ch., 16, 268.

The electric current causes this metal, when in solution as chloride, nitrate, or sulphate, to separate as the dioxide upon the anode (*see* Lead). In a solution of nitric acid, the hydrogen set free reduces the acid to oxides of nitrogen and, finally, to ammonia. Under such conditions complications may arise, particularly if other metals are present in the solution. For this reason a solution of the sulphate, slightly acidulated with two to six drops of sulphuric acid, is preferable for electrolytic purposes. Neumann prefers the mineral acid solutions for these depositions, and gives the following as illustrative examples:

(a) To the solution containing 0.3 gram of manganese nitrate, add 2 c.c. of concentrated nitric acid, dilute to

150 c.c. with water, and electrolyze with $N.D_{100} = 0.3$ ampere and 3–3.5 volts for two hours. It is advisable to add the acid during the course of the electrolysis. When its quantity exceeds 3 per cent. the permanganic acid reaction shows itself.

(b) Add 0.5 c.c. of concentrated sulphuric acid to the solution of 0.3 gram of manganese sulphate, dilute to 150 c.c., heat to 60° – 70° , and act upon the solution for four hours with a current of 0.4–0.6 ampere and 4 volts.

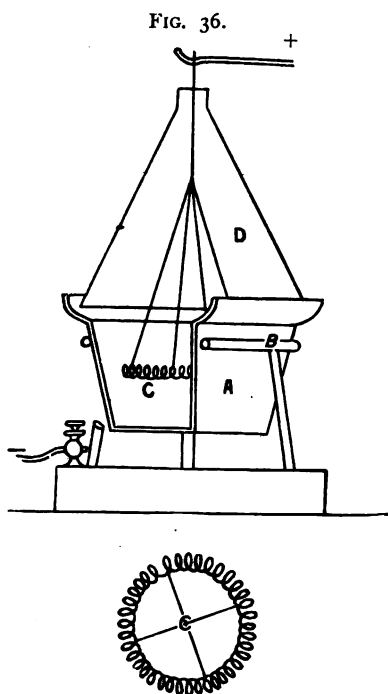
As soon as the manganese has been fully precipitated as dioxide, the current is interrupted, the deposit washed with water, and should any of the dioxide become detached, it must be caught upon a small filter, then dried, ignited, and weighed, together with the adherent dioxide, which is changed to protosesquioxide (Mn_3O_4) before weighing. Groeger has demonstrated by iodometric tests, that the composition of the precipitate only approximates the formula— $MnO_2 \cdot H_2O$ —usually assigned it. Further, it is useless to try to obtain a definite compound by drying. The product is so extremely hygroscopic that ignition alone to the protosesquioxide will give definite and concordant results.

In the presence of large quantities of iron, this precipitation is unsatisfactory; therefore, first remove the iron with barium carbonate. Tartaric, oxalic, and lactic acids retard the formation of manganese dioxide. The same is true of phosphoric acid. Potassium sulphocyanide also prevents its formation, and if added to solutions in which dioxide is already precipitated, it causes the same to redissolve.

Classen maintains that strong mineral acids, such as nitric and sulphuric, retard the complete deposition of the manganese. He regards acetic acid as the most suitable

of all the organic acids for use in this precipitation. The conditions given are: 25 c.c. of acetic acid of specific gravity 1.069; 75 c.c. of water; temperature, 50° – 68° ; $N.D_{100} = 0.3$ – 0.35 ampere; $V = 4.3$ – 4.9 ; time, 3 hours; roughened dish.

Engels dissolves the manganese salt in 50 c.c. of water,



adds 10 grams of ammonium acetate and $1\frac{1}{2}$ –2 grams of chrome alum, then dilutes with water to 150 c.c., heats to 80° , and applies a current of $N.D_{100} = 0.6$ – 0.9 ampere and 3–4 volts. The deposit is washed with water and alcohol, then dried and ignited. The deposition was made in roughened dishes of platinum. Alcohol (5–10 c.c.) may be

substituted for the chrome alum, but more time will then be required for the precipitation.

Kaepfel has given the precipitation of manganese thoughtful consideration. He confirms the experience of Engels, and adds that acetone is a very desirable addition. This method of procedure consists in heating the electrolyte to 55° , adding 1.5 to 10 grams of acetone, and electrolyzing with a current of $N.D_{100} = 0.7-1.2$ amperes and 4-4.25 volts for a period of from two to five hours. The acetone is converted into acetic acid, and it is the transitional formation of the latter that the author regards as more beneficial in the deposition than if it be added directly to the electrolyte.

The apparatus devised by Herpin (Fig. 36) can be well applied in the decomposition of manganese salts. It consists of a platinum dish, *A*, resting upon a tripod, *B*, in connection with the cathode of a battery. The upper portion of the dish is so constructed that it will support an inverted glass funnel, *D*. Any loss from the bursting of bubbles is prevented by this means. The anode is a platinum spiral *C*. In estimating manganese it must not be forgotten to connect the dish with the anode of the battery employed for the decomposition.

IRON.

LITERATURE.—Wrightson, *Z. f. a. Ch.*, 15, 305; Parodi and Masciazini, *G. ch. ital.*, 8, 178; also *Z. f. a. Ch.*, 18, 588; Luckow, *Z. f. a. Ch.*, 19, 18; Classen and v. Reiss, *Ber.*, 14, 1622; Classen, *Z. f. Elektrochem.*, 1, 288; Moore, *Ch. News*, 53, 209; Smith, *Am. Ch. Jr.*, 10, 330. Brand, *Z. f. a. Ch.*, 28, 581; Drown and McKenna, *Jr. An. Ch.*, 5, 627; Smith and Muhr, *Jr. An. Ch.*, 5, 488; Rüdorff, *Z. f. ang. Ch.*, 15. Jahrg., p. 198; Vortmann, *M. f. Ch.*, 14, 536; Heidenreich, *Ber.*, 29, 1585; Avery and Dales, *Ber.*, 32, 64, 2233; Verwer and Groll, *Ber.*, 32, 37, 806; Goecke, *Dissertation*, Bonn, 1900; Kollock, *J. Am. Ch. S.*, 21, 928.

In the historical sketch (p. 54) it was mentioned that Parodi and Mascazzini found that iron could be precipitated from solutions of its double oxalates. This suggestion has since been elaborated by Classen, and by him applied to many other metals. Following the recommendation of this chemist, about six to seven grams of ammonium oxalate are dissolved in as little water as possible, and the iron salt solution gradually added to it with constant stirring. The liquid is then diluted with water to 150–175 c.c., and electrolyzed at the ordinary temperature with a current of $N.D_{100} = 1.5$ amperes and 2–4.5 volts, or at the temperature of 40° – 65° with 0.5–1.0 ampere and 2–3.5 volts. If ferric hydroxide should separate during the electrolytic decomposition, it can be redissolved by adding oxalic acid drop by drop. Test the clear liquid, acidulated with hydrochloric acid, with potassium sulphocyanide. The deposited iron has a steel-gray color; it should be washed with water, alcohol, and ether. Avoid the presence of chlorides and nitrates. By carefully complying with the conditions recommended by Classen good results are sure to follow. To show that persons with but little experience can obtain satisfactory results with the preceding method the two following determinations, made by a student, are given: A quantity of ferric ammonium sulphate ($= 0.0814$ gram of iron) was dissolved in 200 c.c. of water, and to this were added 8 grams of ammonium oxalate. The solution was heated to 80° , and in two hours, with a current of 1.5 amperes, 0.0814 gram of iron was obtained. In a second experiment the quantity of iron was doubled ($= 0.1628$ gram of iron), while the ammonium oxalate was 11 grams, temperature 66° , and the current 1 ampere. The precipitated iron weighed 0.1619 gram instead of 0.1628.

The writer found the following procedure admirably suited for iron determinations: 10 c.c. iron solution (= 0.1277 gram of metal), 10 c.c. sodium citrate (1.8 grams) with 3 c.c. of citric acid (0.059 gram), then diluted with water to 250 c.c., and electrolyzed with a current of $N.D_{100} = 0.8$ ampere and 7-8 volts at 50° for four and one-half hours. The iron deposit weighed 0.1280 gram. It contained 0.94 per cent. of carbon. The deposit was washed as already directed. In several determinations aluminium and titanium were present with the iron, but the latter was precipitated free from the other two. For this reason the writer regards the method as useful. E. F. Kern, working in this laboratory with the view of arriving at some knowledge in regard to the carbon deposition, after long and painstaking experimentation, recommends the following conditions as favorable for the getting of iron deposits free from the carbon impurity: Add 1 gram of sodium citrate and 0.1 gram of citric acid to the solution of iron sulphate (0.1 gram of metal), dilute to 150 c.c., heat to 60° , and electrolyze with $N.D_{100} = 0.8-1.3$ amperes and 9 volts. Just as soon as the iron is precipitated, siphon off the liquid and wash without interruption of the current. The opinion exists that prolonged action of the current after the metal is all deposited tends to increase the carbon content of the iron.

From ammoniacal tartrate solutions iron is also precipitated, but carries carbon with it. It would therefore not be advisable to use this electrolyte except in cases where separations were desired, which were possible only in solutions of this character.

A third method, originated by Moore, advises that glacial phosphoric acid (15 per cent. acid) be added to the distinctly acid solution of ferric chloride or sulphate,

until the yellow color fully disappears, then a large excess of ammonium carbonate is added and a gentle heat is applied until the liquid becomes clear. On electrolyzing the hot (70°) solution with a current of 2 amperes, the iron is rapidly and completely deposited at the rate of 0.75 gram per hour. Avery and Dales, on the other hand, claim that with a current of $N.D_{100} = 2$ amperes and 5 volts they were not able to precipitate more than 0.2 gram of iron in five hours. The end of the decomposition is recognized by testing a portion of the solution with ammonium sulphide. Wash the deposit as already directed.

Recently, quite a little discussion has been had upon the deposition of iron and its enclosures. Avery and Dales question whether the metal is fully precipitated from any one of the electrolytes described in the preceding paragraphs; furthermore, they affirm that even from an oxalate solution the iron carries down carbon with it; that oxalic acid is converted in part, at least, into glycollic acid, and that iron salts in the presence of the latter acid yield upon electrolysis a metal strongly contaminated with hydrocarbons. As to Moore's method, they assert that phosphorus is always present in the deposit of iron. Goecke concurs with these chemists in their views on the cathodic contaminations. Verwer and Groll think that iron, from an oxalate solution, is absolutely free from carbon, while Classen attributes the trifling amounts of carbon, which have been observed, to carelessness and inexperience in the execution of the prescribed directions.

Drown, pursuing a suggestion made by Wolcott Gibbs in 1883 relative to the precipitation of metals in the form of amalgams, has applied it to the determination of iron. The trial tests were made with a solution of ferrous ammonium sulphate, slightly acidulated with sulphuric acid, to

which a large excess of mercury was added (not less than fifty times the weight of the iron to be precipitated). A large platinum anode was used, while the mercury cathode was brought into the circuit by means of a platinum wire enclosed and fused into one end of a glass tube which passed through the liquid. The current employed for the precipitation equaled about 2 amperes per minute. The author remarks that if these conditions be observed, as much as 10 grams of iron can be precipitated in from ten to fifteen hours.

The decomposition was carried out in beaker glasses. Care should be exercised in drying, so that no mercury is volatilized.

URANIUM.

LITERATURE.—Luckow, *Z. f. a. Ch.*, 19, 18; Smith, *Am. Ch. Jr.*, 1, 329; Smith and Wallace, *J. Am. Ch. S.*, 20, 279; Kollock and Smith, *J. Am. Ch. S.*, 23, 607; Kern, *J. Am. Ch. S.*, 23, 685.

For electrolytic purposes use the acetate, the sulphate, or the nitrate. Connect the dish in which the deposition is made with the negative electrode of the battery. The uranium separates as yellow uranic hydroxide upon the cathode; by the continued action of the current it changes to the black hydrated protos(es)quioxide. As soon as the solution becomes colorless, interrupt the current, wash with a little acetic acid and boiling water; dry, ignite, and weigh as protos(es)quioxide. If any of the hydrate becomes detached, collect the same upon a small filter, and ignite the latter together with the dish contents. Conditions leading to successful results are contained in the following examples:—

ELECTROLYSIS OF URANIUM ACETATE.

U ₃ O ₈ PRESENT, IN GRAMS.	29 PER CENT ACETIC ACID. CC.	DILUTION. C.C.	CURRENT.	VOLTS.	TEMPERATURE. °C.	TIME. HOURS.	U ₃ O ₈ FOUND, IN GRAMS.	ERROR IN GRAMS.
0.0986	0.2	125	N.D. ₁₀₇ = 0.29 A	16.25	70	5	0.0988	+0.0002
0.0986	0.2	125	N.D. ₁₀₇ = 0.3 A	12.2	70	5	0.0989	+0.0003
0.1972	0.2	125	N.D. ₁₀₇ = 0.3 A	10.75	70	6	0.1970	-0.0002
0.2298	0.1	125	N.D. ₁₀₇ = 0.09 A	4.25	70	6	0.2297	-0.0001
0.2298	0.2	125	N.D. ₁₀₇ = 0.07 A	4.25	70	5½	0.2299	+0.0001

ELECTROLYSIS OF URANYL NITRATE SOLUTIONS.

U ₃ O ₈ PRESENT, IN GRAMS.	DILUTION. C.C.	TEMPERATURE. °C.	CURRENT.	VOLTS.	TIME. HOURS.	U ₃ O ₈ FOUND, IN GRAMS.
0.1222	125	75	N.D. ₁₀₇ = 0.035 A	4.6	5½	0.1225
0.1222	125	65	N.D. ₁₀₇ = 0.04 A	2.25	7½	0.1218

Quantitative results were also obtained by the electrolysis of the sulphate. The neutral salt solution was diluted to 125 c.c. and heated to 75° C., when a current of from 0.02 to 0.04 ampere for 107 sq. cm. of cathode surface and 2.25 volts was conducted through the liquid.

ELECTROLYSIS OF URANYL SULPHATE.

U ₃ O ₈ PRESENT, IN GRAMS.	DILUTION. C.C.	TEMPERATURE. °C.	CURRENT.	VOLTS.	TIME. HOURS.	U ₃ O ₈ FOUND, IN GRAMS.	ERROR IN GRAMS.
0.1320	125	75	N.D. ₁₀₇ = 0.02 A	2	6½	0.1320	...
0.1320	125	75	N.D. ₁₀₇ = 0.02 A	2	5½	0.1322	+0.0002
0.1393	125	75	N.D. ₁₀₇ = 0.04 A	2.25	5	0.1395	+0.0002
0.1393	125	70	N.D. ₁₀₇ = 0.038 A	2.25	7	0.1392	-0.0001

This method affords an excellent separation of uranium from the alkali and alkaline earth metals (p. 191).

THALLIUM.

LITERATURE.—Schucht, *Z. f. a. Ch.*, 22, 241, 490; Neumann, *Ber.*, 21, 356.

This metal separates as sesquioxide, from acid solutions, upon the anode, while from ammoniacal liquids it is deposited partly as metal and partly as oxide. From oxalate solutions and from its double cyanides it separates only as metal when the current is feeble. However, difficulty is experienced in drying the deposit without having it oxidized. In this respect it is even more troublesome than lead. Neumann utilizes the current to separate the metal, dissolves the latter in acid, and measures the liberated hydrogen; from its volume he calculates the quantity of thallium originally present. For suitable apparatus to carry out this method consult the literature cited above.

PLATINUM.

LITERATURE.—Luckow, *Z. f. a. Ch.*, 19, 13; Classen, *Ber.*, 17, 2467; Smith, *Am. Ch. Jr.*, 13, 206; Rüdorff, *Z. f. ang. Ch.*, 1892, 696.

The solutions of platinum salts, slightly acidulated with sulphuric acid, and acted upon by a feeble current, give up the metal as a bright, dense deposit upon the dish, frequently so light as to be scarcely distinguished from the latter. In using platinum vessels for this purpose, first coat them with a rather thick layer of copper, upon which afterward deposit the metal. Wash the deposit with water and alcohol.

In ordinary gravimetric analysis, potassium is frequently estimated as potassio-platinum chloride, K_2PtCl_6 . This operation requires time and care. Rather dissolve the double salt in water, slightly acidulate the solution with sulphuric acid (2 to 3 per cent. by volume), and electrolyze with a current of $N.D_{100} = 0.1-0.2$ ampere. The deposit will be spongy. On heating to $60^{\circ}-65^{\circ}$ and electrolyzing with $N.D_{100} = 0.05$ ampere and 1.2 volts, the platinum will be completely precipitated in from four to five hours in a perfectly adherent form. It is often so dense as to be distinguished from hammered platinum with difficulty.

In the Munich laboratory the platinum salt solution is mixed with 2 per cent. (by volume) of a dilute sulphuric acid (1 : 5), heated to 70° , and electrolyzed with $N.D_{100} = 0.01-0.03$ ampere. The precipitation will be complete in five hours.

The following experiment executed in this laboratory demonstrates that the precipitation of platinum from solutions containing sodium phosphate and free phosphoric acid is complete. The volume of the liquid was 150 c.c. It contained 0.1144 gram of metallic platinum, 30 c.c. of disodium hydrogen phosphate (sp. gr. 1.0358), and 5 c.c. of phosphoric acid (sp. gr. 1.347). The current equaled 0.8 ampere. The deposit of platinum weighed 0.1140 gram. It was precipitated upon a copper-coated platinum dish. It was washed with water and alcohol. Ten hours were required for the deposition.

PALLADIUM.

LITERATURE.—Wöhler, *Ann.*, **143**, 375; Schucht, *Z. f. a. Ch.*, **22**, 242; Smith and Keller, *Am. Ch. Jr.*, **12**, 252; Smith, *Am. Ch. Jr.*, **13**, 206; **14**, 435; Joly and Leidié, *C. r.*, **116**, 146; *Z. f. anorg. Ch.*, **3**, 476.

Palladium can be deposited from solutions of the same kind and in the same manner as platinum. A bright metallic deposit will be obtained by the use of a current of $N.D_{100} = 0.05$ ampere and 1.2 volts; otherwise it is spongy.

It has been discovered, in this laboratory, that this metal can be rapidly and fully precipitated from ammoniacal solutions of palladammonium chloride, $Pd(NH_3Cl)_2$, which may be prepared by adding hydrochloric acid to an ammonium hydroxide solution of palladious chloride. To show the accuracy of this method, several actual determinations are here introduced: (1) A quantity of the double salt (= 0.2228 gram of palladium) was dissolved in ammonium hydroxide; to this solution were added 20–30 c.c. of the same reagent (sp. gr. 0.935) and 100 c.c. of water. A current of 0.07–0.1 ampere acted upon this mixture through the night, and deposited 0.2225 gram of palladium. (2) In another experiment, with conditions similar to those just mentioned, excepting that the quantity of the palladammonium chloride was doubled, and the current held at 0.7 ampere, the quantity of metal precipitated equaled 0.4462 gram instead of 0.4456. Oxide did not separate upon the anode. The deposit, when dry, showed the same appearance as is ordinarily observed with this metal in sheet form. It was washed with hot (70°) water, and dried in an air-bath at 110°–115°. It is best to deposit the palladium in platinum dishes previously coated with silver.

RHODIUM.

LITERATURE.—Smith, Jr. An. Ch., 5, 201; Joly and Leidié, C. r., 112, 793.

Few attempts have been made to determine this metal electrolytically. Its separation from an acid phosphate solution is very rapid and complete. A current of 0.18 ampere will answer perfectly for the purpose. As the decomposition progresses, the beautiful purple color of the liquid gradually disappears, and the solution is colorless when the precipitation is finished. The deposition of the rhodium should be made upon copper-coated dishes. The metal is generally black in color, very compact, and perfectly adherent. Hot water may be used for washing purposes.

Joly precipitates the metal from solutions acidulated with sulphuric acid.

MOLYBDENUM.

LITERATURE.—Smith, Am. Ch. Jr., 1, 329; Hoskinson and Smith, *ibid.*, 7, 90; Kollock and Smith, J. Am. Ch. S., 23, 669.

When the electric current acts upon ammoniacal or feebly acid solutions of ammonium molybdate, a beautiful iridescence appears; as the action continues this assumes a black color, and the deposit becomes more dense. It is the hydrated sesquioxide which is precipitated. At the time when these observations were made, experiments were instituted to determine the metal. The results, while quantitative in character, were obtained with the

consumption of too much time to permit of the method being generally applied. Recently attention has again been given to the subject in this laboratory. Sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) was dissolved so that 0.1302 gram of molybdenum trioxide was present in 125 c.c. of solution, which was exposed for several hours to the action of a current of 0.1 ampere and 4 volts. The temperature of the electrolyte was 75°C . No precipitation occurred upon either electrode. Upon adding two drops of concentrated sulphuric acid to the liquid, it at once assumed a dark blue color. As the current continued to act, this color disappeared and the cathode was coated with a black deposit—the hydrated sesquioxide. On removing the colorless liquid and testing it with ammonium thiocyanide, zinc, and hydrochloric acid, evidences of the presence of molybdenum failed to appear. The deposit was brilliant black in color and so adherent that it could be washed without detaching any particles. Usually the colorless liquid was removed with a siphon, cold water being introduced without interrupting the current. The deposit was not dried, but dissolved while moist from off the dish in dilute nitric acid, and the solution carefully evaporated to dryness, the residue being heated upon an iron plate to expel the final traces of acid. White molybdic acid remained. If blue spots appeared in the mass, they were removed by moistening the residue with nitric acid and evaporating a second time to dryness. This procedure was adopted in all the experiments. It was not possible to obtain concordant results by merely drying the hydrate at a definite temperature. The same was true in regard to the ignition of the hydrate to trioxide. Loss occurred from sublimation and volatilization.

RESULTS.

	MOLYBDENUM TRIOXIDE PRESENT, IN GRAMS.	SULPHURIC ACID ADDED, C.C.	DILUTION, C.C.	TEMPERATURE, °C.	CURRENT.	VOLTS.	TIME, HOURS.	MOLYBDENUM TRIOXIDE FOUND, IN GRAMS.	ERROR, IN GRAMS.
1	0.1302	0.1	125	70	N.D. ₁₀₇ = 0.022 A	2.0	4 $\frac{3}{4}$	0.1299	—0.0003
2	0.1302	0.1	125	80	N.D. ₁₀₇ = 0.045 A	2.25	2 $\frac{1}{2}$	0.1302	. . .
3	0.1302	0.1	125	70	N.D. ₁₀₇ = 0.04 A	2.2	4 $\frac{1}{2}$	0.1302	. . .
4	0.2604	0.2	125	75	N.D. ₁₀₇ = 0.04 A	2.0	7	0.2603	—0.0001
5	0.1541	0.2	125	85	N.D. ₁₀₇ = 0.04 A	1.9	2 $\frac{1}{2}$	0.1541	. . .
6	0.1541	0.2	125	80	N.D. ₁₀₇ = 0.035 A	2.1	4	0.1540	—0.0001

The method is accurate, is easy of execution, and requires comparatively little time.

It seemed that the method could be made useful in the determination of the molybdenum content of the mineral molybdenite. By fusing the latter with a mixture of pure alkaline carbonate and nitrate, sodium molybdate and sulphate would be formed. If the sulphur is not to be determined, after dissolving out the fusion with water, and filtering off the insoluble oxides, acidulate the alkaline liquid with dilute sulphuric acid and proceed with the electrolysis; but in cases where an estimation of the sulphur is desired, it was thought that acetic acid would answer for the purpose of acidulation. To ascertain the latter fact the experiments given below were instituted. The solution, acidified with this acid, does not acquire a blue color on passing the current through it. The deposit of hydrated oxide is very adherent and readily washed. A longer time is necessary for the complete precipitation. It is also advisable not to add the entire volume of acetic acid at first, but to introduce it gradually from time to time, from a burette.

RESULTS.

	MOLYBDENUM TRIOXIDE PRESENT, IN GRAMS.	20 PER CENT. ACETIC ACID ADDED, C.C.	DILUTION, C.C.	TEMPERATURE, °C.	CURRENT.	VOLTS.	TIME, HOURS.	MOLYBDENUM TRIOXIDE FOUND, IN GRAMS.	ERROR, IN GRAMS.
1	0.1541	1	125	85	$N.D_{107} = 0.075$ A	4.4	7½	0.1541	...
2	0.1541	1	125	85	$N.D_{107} = 0.075$ A	4.4	3	0.1540	- 0.0001
3	0.1541	1	125	80	$N.D_{107} = 0.05$ A	2.5	6	0.1543	+ 0.0002

In the last experiment, 5 grams of sodium acetate were added in order to increase the conductivity of the solution and to ascertain what effect an excess of this salt would have, because, if the acetic acid were used to acidify the alkaline solution obtained by the decomposition of molybdenite, a great deal of this salt would be present. The concordant results justified the next step, which was to decompose weighed amounts of pulverized molybdenite with sodium carbonate and nitrate, then take up the fusion with water, filter out the insoluble oxides, acidify with acetic acid, boil off the carbon dioxide, and electrolyze. The liquid poured off from the deposit of the sesquihydroxide was heated to boiling and precipitated with a hot solution of barium chloride.

	MOLYBDENITE, IN GRAMS.	MOLYBDENUM FOUND, IN PER CENT.	SULPHUR FOUND, IN PER CENT.
1	0.2869	57.37	38.28
2	0.1005	57.15	38.33
3	0.1388	56.83	37.87

GOLD.

LITERATURE.—Luckow, *Z. f. a. Ch.*, 19, 14; Brugnattelli, *Phil. Mag.*, 21, 187; Smith, *Am. Ch. Jr.*, 13, 206; Smith and Muhr, *Am. Ch. Jr.*, 13, 417; Smith, *Jr. An. Ch.*, 5, 204; Smith and Wallace, *Ber.*, 25, 779; Frankel, *Jr. Fr. Ins.*, 1891; Persoz, *Ann. Chim. Pharm.*, 65, 164; Rüdorff, *Z. f. ang. Ch.*, 1892, p. 695.

This metal can be completely deposited from solutions containing it in the form of a double cyanide, sulphaurate, and sulphocyanide, as well as in the presence of free phosphoric acid. In this laboratory the cyanide and sulphaurate have received the most consideration. An example will illustrate the conditions with which good results may be obtained from the double cyanide: A solution contained 0.1162 gram of metallic gold; to it were added 1.5 grams of potassium cyanide and 150 c.c. of water. It was heated to 55° and electrolyzed with a current of $N.D_{100} = 0.38$ ampere and 2.7–3.8 volts. The precipitation was complete in one and one-half hours. The gold deposit weighed 0.1163 gram. It was washed both with cold and hot water. The metal may be precipitated upon silver-coated or copper-coated platinum vessels, or directly upon the sides of the platinum dish. If the last suggestion is followed, dissolve off the gold, after weighing, by introducing very dilute potassium cyanide into the dish, and then connect the latter with the anode of a battery yielding a very feeble current.

The deposition of gold from a sodium sulphide solution (sp. gr. 1.18) is just as satisfactory as that described in the last paragraph. The current should equal 0.1–0.2 ampere for a total dilution of about 125 c.c. The precipitated metal is very adherent and of a bright yellow color.

The facts relating to the electrolytic behavior of vana-

dium (Truchot, *Ann. Chim. Anal.* (1902), **7**, 165-167), tungsten, and osmium are, at the present writing, few in number and will not be given here.

TIN.

LITERATURE.—Luckow, *Z. . a. Ch.*, **19**, 13; Classen and v. Reiss, *Ber.*, **14**, 1622; Gibbs, *Ch. News*, **42**, 291; Classen, *Ber.*, **17**, 2467; **18**, 1104; Bongartz and Classen, *Ber.*, **21**, 2900; Rüdorff, *Z. f. ang. Ch.*, **1892**, 199; Classen, *Ber.*, **27**, 2060; Engels, *Z. f. Elektrochem.*, **2**, 418; Freudenberg, *Z. f. ph. Ch.*, **12**, 121; Heidenreich, *Ber.*, **28**, 1586; Campbell and Champion, *J. Am. Ch. S.*, **20**, 687; Klapproth, *Dissertation*, Hannover, 1901; Classen, *Z. f. Elektrochem.*, **1**, 289.

Tin may be deposited from a solution of ammonium tin oxalate. It is advisable not to use potassium oxalate in the electrolysis, for then a basic salt is liable to separate upon the anode.

Classen adds 120 c.c. of a saturated ammonium oxalate solution to the liquid containing 0.9-1.0 gram of stannic ammonium chloride, then electrolyzes at 30°-35° with a current of 0.3-0.6 ampere and 2.8-3.8 volts. Acid ammonium oxalate must be added from time to time if large quantities of metal are to be precipitated. The tin separates in a brilliant, white, adherent form. It is washed and dried in the usual way. The time required for precipitation is generally nine hours. This factor, however, can be reduced, as is evident from the following example: Acidulate the solution containing 0.4 gram of tin and 4 grams of ammonium oxalate with 9-10 grams of oxalic acid; heat to 60°-65°, and electrolyze with $N.D_{100} = 1-1.5$ amperes. Acetic acid may replace the oxalic acid. Fusion with potassium acid sulphate will remove the tin from the dish.

Campbell and Champion use the oxalate method in determining tin in its ores. Fuse 1 gram of the ore with 5–6 grams of a mixture of equal parts of soda and sulphur for an hour and a half, at full red heat. This is done in a porcelain crucible, placed within a second crucible of the same material. Dissolve the sulphostannate in from 40–50 c.c. of hot water, filter, and re-fuse the residue as before. Add hydrochloric acid, to faint acid reaction, to the combined solutions of sulpho-salts. Stannic sulphide will be precipitated. Boil off the hydrogen sulphide, add 10 c.c. of hydrochloric acid (sp. gr. 1.20), and then gradually introduce 2–3 grams of sodium peroxide until a clear liquid is obtained. Boil for three minutes, filter out the separated sulphur, add ammonia water to permanent precipitation and 50 c.c. of a 10 per cent. acid ammonium oxalate solution. Electrolyze with a current of $N.D_{100} = 0.1$ ampere and 4 volts. Allow the current to act through the night. The deposit will be light in color and very adherent.

Classen has discovered that a tin solution containing an excess of ammonium sulphide, largely diluted with water, yields a quantitative deposition of the metal when exposed to the action of a current from two Bunsen cells. In dilute sodium or potassium sulphide solution the tin precipitation is incomplete, and whenever such conditions exist, the sodium or potassium salt must be converted into ammonium sulphide. To this end the liquid is mixed with about 25 grams of ammonium sulphate, free from iron, and the solution then carefully warmed in a covered vessel until the evolution of hydrogen sulphide ceases; after which the liquid is heated to incipient ebullition for fifteen minutes. Allow it to cool, dissolve any sodium sulphate which may have separated by the addition of

water, and electrolyze. The tin separates in a gray, dense layer. Wash it with water and alcohol. At times sulphur sets itself upon the tin deposit; this is difficult to remove, but can be detached, after washing the deposit with alcohol, by gently applying a linen handkerchief. Having potassium sulphostannate, Classen considers it advisable to convert the tin into oxalate and then electrolyze. He employs two methods. One will be given here:—

Decompose the greater portion of the sulpho-salt with dilute sulphuric acid (the liquid must remain alkaline) to get rid of most of the sulphur as hydrogen sulphide, then oxidize with hydrogen peroxide until the metastannic acid produced is pure white in color. Acidulate with sulphuric acid, neutralize with ammonia water, and again add hydrogen peroxide. Filter out the stannic acid when it has subsided, dissolve in oxalic acid and ammonium oxalate, and electrolyze with the conditions given in the preceding paragraphs.

According to Carl Engels add 0.3 to 0.5 gram of hydroxylamine hydrochloride or sulphate, 2 grams of ammonium acetate, and 2 grams of tartaric acid to the solution of the tin salt, dilute with water to 150 c.c., heat to 60°–70°, and electrolyze with $N.D_{100} = 1$ ampere.

ANTIMONY.

LITERATURE.—Wrightson, Z. f. a. Ch., 15, 300; Parodi and Mascarzini, Z. f. a. Ch., 18, 588; Luckow, Z. f. a. Ch., 19, 13; Classen and v. Reiss, Ber., 14, 1622; 17, 2467; 18, 1104; Lecrenier, Ch. Z., 13, 1219; Chittenden, Pro. Conn. Acad. Sci., Vol. 8; Vortmann, Ber., 24, 2762; Rüdorff, Z. f. a. Ch., 1892, 199; Classen, Ber., 27, 2060; Ost and Klaproth, Z. f. ang. Ch. (1900), 827.

Antimony, when precipitated from a solution of its chloride, or from that of antimony potassium oxalate, does not adhere well to the cathode. It is deposited very slowly from a solution of potassium antimonyl tartrate. Its deposition from a *cold* ammonium sulphide solution is satisfactory, but the use of this reagent for this purpose is not pleasant, especially when several analyses are being carried out simultaneously. For this reason potassium or sodium sulphide has been substituted. The alkaline sulphide used must not contain iron or alumina.

The antimony solution, mixed with 80 c.c. of sodium sulphide (sp. gr. 1.13–1.15), should be diluted with water to 125 c.c. and acted upon at 60°–65° with a current of $N.D_{100} = 1$ ampere and 1.1–1.7 volts. The metal will be fully precipitated in two hours. The deposit should be treated in the usual way with water and pure alcohol. Dry at 90°. To ascertain when all of the metal has been deposited, incline the dish slightly, thus exposing a clean platinum surface. If this remains bright for half an hour the precipitation is finished. In separating antimony from the heavy metals—*e. g.*, lead—it happens that alkaline sulphides containing polysulphides are used, or are produced. To remove these Classen proposed adding to the antimony-polysulphide mixture, already in a weighed platinum dish, an ammoniacal solution of hydrogen per-

oxide, and warming the same until the liquid becomes colorless. When this is accomplished, even if a precipitate has been produced, add, after cooling, the solution of sodium monosulphide, and electrolyze as previously directed.

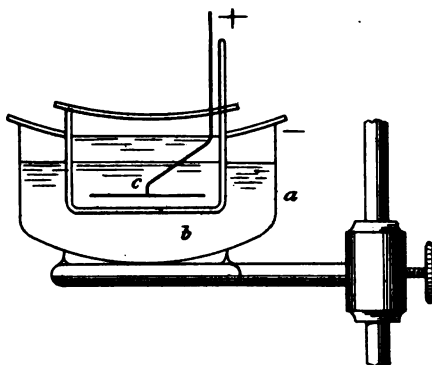
Lecrenier writes as follows relative to the preceding method: The precipitation is all that one can desire, providing the solution of the sulpho-salt is absolutely free from polysulphides; otherwise, it is incomplete. The antimony sulphide obtained in the ordinary course of analysis always contains sulphur, and this must be eliminated. To remove the various inconveniences connected with the method add 50–70 c.c. of a 25 per cent. solution of sodium sulphite to the solution after the addition of the excess of sodium sulphide, then heat the liquid to complete decolorization; allow to cool, after which the current is conducted through the liquid. This can rise to 0.5 ampere without impairing the result; but it is not best, as the precipitated metal is then not very coherent. It is better to use a current of 0.25 ampere. When the quantity of antimony does not exceed 0.2 gram, the deposit will be adherent and free from sulphur; wash with water, alcohol, and ether. Sulphur will separate upon the anode, despite the presence of an excess of sodium sulphite. This, however, does not affect the result.

The method of Classen suffers in several points:

1. The bath pressure falls as the electrolysis proceeds, because of the accumulation in it of sodium polysulphide.
2. If the electrolysis is not interrupted at the proper moment, antimony already precipitated will be again dissolved by the polysulphide which has diffused toward the cathode (*Z. f. ang. Ch.*, 1897, 325). Ost and Klapproth have sought by the use of a diaphragm to circumvent

these objectionable features. To this end they use (Fig. 37) a roughened dish, *a*, in which is suspended a dish-shaped diaphragm, *b* (a Pukall porous cup, Ber., 26, 1159). A strip of platinum, *c*, within the diaphragm, is the anode, while the platinum dish itself constitutes the cathode. Cover-glasses are placed over both dishes. The liquids

FIG. 37.



experimented upon were a solution of Schlippe's salt (= 0.0985 gram of antimony in 10 c.c.) and a solution of pure sodium sulphide (195 grams Na_2S = 200 grams NaOH to the litre). In the first experiments the antimony was equally distributed in the whole electrolyte. The cathode chamber contained 85 c.c. and the anode chamber 40 c.c. of the solution, which had 0.0985 gram of antimony in 125 c.c., with varying amounts of sodium

sulphide. The liquid covered about 100 sq. cm. of the surface of the dish:—

EXPERIMENT.	Na ₂ S SOLUTION.	TEMPERATURE.	BATH PRESSURE AT 1 AMPERE.		CURRENT STRENGTH IN AMPERES.		ANTIMONY PRECIPITATED.
			BEGINNING VOLTS.	END VOLTS.	AT BEGINNING.	AT END.	
1	5 c.c.	70°	3.8	3.9	0.7	0.3	0.0675
2	50 "	Cold	1.9	3.8	0.5	0.4	0.0725
3	80 "	70°	2.5	1.7	1.0	1.0	0.0685
4	80 "	70°	1.7	1.3	1.0	1.0	0.0720

When the electrolysis was finished, antimony could not be found in the cathode liquid from any one of the four experiments, whereas in the anode chamber it was still in solution, and in experiment 1 it had been precipitated on the anode in the form of antimony pentasulphide.

These experiments indicated then that the current is not able to carry antimony ions from the anode into the cathode chamber.

In the next series of experiments the 10 c.c. of antimony solution (= 0.0985 gram of metal) were placed in the cathode chamber alone:—

EXPERIMENT.	Na ₂ S SOLUTION.	TEMPERATURE.	BATH PRESSURE AT 1 AMPERE.		TIME.	ANTIMONY PRECIPITATED.
			BEGINNING VOLTS.	AT END VOLTS.		
1	50	Cold	4.2	3.7	5 hours	0.0970
2	50	70°	2.0	3.8	3 "	0.0984
				Temp. 32°		
3	80	70°	2.5	1.7	2 "	0.0990
4	50	70°	1.8	1.8	1½ "	0.0990

The results show a quantitative precipitation of the antimony. None of it could be found either in the cathode or anode liquid.

On placing the antimony in the anode chamber alone, not a particle of metal was deposited on the cathode.

When the antimony was placed in the cathode chamber only and varying quantities of sodium sulphide solution were mixed with it, remarkable differences were observed. In the presence of much sodium sulphide and accompanying low bath pressure all of the antimony was precipitated at the cathode, while with little sodium sulphide and consequent high bath pressure, a small amount of antimony wandered through the diaphragm and was deposited at the anode in the form of antimony sulphide.

These experiments show how a successful antimony determination may be made. No difficulties attend its estimation in this way.

Vortmann, recognizing the fact that it is difficult to obtain an adherent deposit of antimony when the quantity of metal in solution exceeds 0.16 gram, has combined the method of Smith, who first pointed out that mercury could be deposited very satisfactorily from its solution in sodium sulphide, with his knowledge that antimony could be precipitated from a similar solution, and hence recommends the determination of the antimony in the form of an amalgam. No difficulties attend this procedure. Two parts of mercury should be present for every part of antimony. The latter must also be present in solution as higher oxide; to this end digest the antimonious solution with bromine water, and afterward add the sodium sulphide containing sodium hydroxide. Electrolyze with a current of from 0.2 to 0.3 ampere. The amalgam can be washed in the usual way.

ARSENIC.

LITERATURE.—Luckow, *Z. f. a. Ch.*, 19, 14; Classen and v. Reiss, *Ber.*, 14, 1622; Moore, *Ch. News*, 53, 209; Vortmann, *Ber.*, 24, 2764.

A successful method for the complete deposition of arsenic is not known. The current acting upon the chloride causes complete volatilization of the metal in the form of arsine. Its separation from oxalate solutions is incomplete; nor do the sulpho-salts answer for electrolytic purposes.

From a solution containing 0.2662 gram of arsenious oxide Vortmann obtained 0.18527 gram of metallic arsenic, equivalent to 69.59 per cent. The trioxide contains 75.78 per cent. of arsenic. This precipitation was effected by the amalgam method.

2. SEPARATION OF THE METALS.

Electrolysis, to be of value, must not only furnish the analyst with methods suitable for the complete deposition of metals, but it should, in addition, enable him to separate metallic mixtures. The data given in the preceding pages will serve for this purpose, but, as a special treatment is required in some instances, a brief outline of a series of separations will be indicated.

It will be noticed that the electrolytes vary. The mineral acid and the double cyanide solutions are best adapted for the purpose. The greatest number of separations have been made by means of them. Some of the organic acids, too, answer quite well as will be seen in the succeeding paragraphs.

COPPER.

Inasmuch as the electrolytic precipitation of copper gives the analyst such an excellent means of determining this metal quantitatively, its separations from other metals are of prime importance. Such separations, so far as they have been carefully worked out in the most essential points, are given in detail in the following paragraphs. It is needless to add that acid solutions mainly are best adapted for these separations.

1. From Aluminium:—

- (a) *In nitric acid solution.* Dilution, 200 c.c.; 5 c.c. of nitric acid (sp. gr. 1.30); temperature, 32°; $N.D_{100} = 1$ ampere and 3.3 volts; time, 4 hours.
- (b) *In sulphuric acid solution.* Dilution, 150 c.c.; 3 c.c. of concentrated sulphuric acid; temperature, 59°; $N.D_{100} = 1$ ampere and 2.5 volts; time, 2 hours.
- (c) *In phosphoric acid solution.* Dilution, 225 c.c.; 5 c.c. of phosphoric acid (sp. gr. 1.347); temperature, 77° C.; $N.D_{100} = 0.068$ ampere and 2.6 volts; time, 6 hours. Sixty cubic centimetres of disodium hydrogen phosphate (sp. gr. 1.0338) were present for 0.1239 gram of copper and 0.1000 gram of aluminium. The precipitated copper weighed 0.1240 gram (J. Am. Ch. S., 21, 1002).

2. From Antimony:—

In tartrate solution. In the presence of one-tenth of a gram of each metal, making certain that the antimony is in its highest state of oxidation, add 8 grams of tartaric acid and 30 c.c. of ammonia (sp. gr. 0.91). Electrolyze at 50° with a current of $N.D_{100} = 0.08-0.10$ ampere and 1.8-2 volts. Total dilution 150 c.c.

The ordinary temperature. Time, 5 hours (J. Am. Ch. S., 15, 195).

Smith and Wallace (Jr. An. Ch., 7, 189; Z. f. anorg. Ch., 4, 274) have also used this separation with eminent success. They, too, emphasize the necessity of having the antimony in its highest form of oxidation. Several examples will illustrate their method of procedure:—

COPPER PRES- ENT, IN GRAMS.	ANTI- MONY, IN GRAMS.	DILU- TION.	VOL. OF AMMONIA (SP. GR. 0.932).	TAR- TARIC ACID, IN GRAMS.	VOLTS.	N.D ₁₀₀ = AMP.	COPPER FOUND.
0.0670	0.1449	175 c.c.	15 c.c.	3-4	1.8	0.1	0.0670
0.1341	0.1449	175 "	15 "	3-4	2.0	0.1	0.1341
0.1341	0.2898	175 "	15 "	3-4	2.0	0.08	0.1344

The deposited metal showed no antimony.

3. From Arsenic:—

(a) *In ammoniacal solution.* McCay (Ch. Z., 14, 509) observed that a current conducted through a potassium arsenate solution, made distinctly ammoniacal, had no effect upon the arsenic, while with copper under like conditions the metal was quantitatively precipitated. Upon this behavior he has based a very excellent separation of the two metals. Care should be taken not to introduce too much ammonia water. In this laboratory the method of McCay, with the conditions here presented, has repeatedly given excellent results:—

Add 20 c.c. of ammonium hydroxide (sp. gr. 0.91) and 2.5 grams of ammonium nitrate to the solution containing 0.2121 gram of copper and 0.1540 gram of

arsenic; dilute to 125 c.c. with water, heat to 50° – 60° , and electrolyze with $N.D_{100} = 0.5$ ampere and 3.5 volts. The copper, precipitated in three hours, weighed 0.2123 and 0.2121 gram. Drossbach (Ch. Z., 16, 819) and Oettel confirm (Ch. Z. (1890), 14, 509) (*also see* Copper) McCay's experience.

Freudenberg, who adopted the suggestion of Kili-ani, of giving more attention to the pressure than to the amperage, succeeded in separating copper and arsenic (latter existing as arsenate) by arranging to have in their solution, 30 c.c. in excess of a 10 per cent. ammonia solution and then electrolyzing with a current of 1.9 volts until the liquid became colorless, which usually occurred after from 6–8 hours (Z. f. ph. Ch., 12, 118).

Schmucker separated copper from arsenic with conditions similar to those indicated for copper and antimony in ammoniacal tartrate solution (see above).

- (b) *In potassium cyanide solution.* Add the copper solution to that of the alkaline arsenite or arsenate, and then introduce a solution of potassium cyanide until the precipitate first produced is just dissolved; the liquid will then show a slight purple tint. Electrolyze with the following conditions: $N.D_{100} = 0.25$ – 0.26 ampere; volts = 3.4–3.6; dilution, 150 c.c.; time, 3 hours; temperature, 60° .
- (c) *In acid solution.* Freudenberg adds 10–20 c.c. of dilute sulphuric acid to the solution of the metals in question and then electrolyzes with a current having a tension of 1.9 volts. The arsenic existed partly as trioxide and partly as pentoxide. The precipitation was made during the night (Z. f. ph. Ch., 12, 117). Copper present, 0.3000 gram; found, 0.2997

gram; arsenic present, 0.3531 gram. The copper was always brilliant in color.

The separation can also be made in nitric acid solution with the same voltage. It is inferior to the first method.

4. **From Barium, Strontium, Calcium, Magnesium, and the Alkali Metals.** The conditions given for the separation of copper from aluminium in nitric acid solution (p. 121) will serve for its separation from these metals.

5. **From Bismuth.** See the separation of bismuth from copper, p. 158.

6. **From Cadmium:—**

(a) *In nitric acid solution.* It was in a solution containing free nitric acid that these two metals were first separated electrolytically (Am. Ch. Jr., 2, 41). The results have been frequently confirmed. An idea of the proper working conditions may be obtained from the following: To a solution in which were present 0.0988 gram of copper and 0.1152 gram of cadmium were added 2 c.c. of nitric acid of sp. gr. 1.43. The total dilution of the liquid equaled 100 c.c. It was heated to 50° and electrolyzed with $N.D_{100} = 0.10$ ampere and 2.5 volts. In 3 hours the copper was completely precipitated. It was bright in color and weighed 0.0988 gram. It contained no cadmium (J. Am. Ch. S., 19, 873; also Jr. An. Ch., 7, 253).

When the copper has been precipitated, washed, dried, and weighed, make the residual liquid alkaline with sodium hydroxide, add sufficient potassium cyanide to redissolve the precipitate, and electrolyze as directed on p. 68.

(b) *In sulphuric acid solution.* From solutions in which there is free sulphuric acid the copper may be

electrolytically precipitated, leaving the cadmium. This is evidenced by the following examples: Total dilution, 100 c.c.; 10 c.c. of sulphuric acid, sp. gr. 1.09; 0.1975 gram of copper and 0.1828 gram of cadmium; $N.D_{100} = 0.05-0.07$ ampere and 1.70-1.76 volts; at the ordinary temperature. The precipitate of copper weighed 0.1976 gram (Am. Ch. Jr., 12, 110). By heating the electrolyte the time can be reduced to 8 hours.

The separation has also been made by strict attention to difference in potential (Freudenberg, Z. f. ph. Ch., 12, 116). Ten to twenty cubic centimetres of dilute sulphuric acid are added to the solution containing the two metals and the liquid is then electrolyzed with a current not exceeding 2 volts. The copper will be deposited very rapidly and be free from cadmium.

COPPER TAKEN.	CADMIUM TAKEN.	COPPER FOUND.
0.2734 gram	0.2560 gram	0.2729 gram
0.4101 "	0.2958 "	0.4098 "
0.3000 "	0.4437 "	0.3003 "

These separations were conducted during the night. Heidenreich (Ber., 29, 1585) met with success in applying Freudenberg's suggestion, but asserts that the tension should not exceed 1.8 volts for $N.D_{100} = 0.07-0.05$ ampere.

- (c) *In phosphoric acid solution.* The separation of the two metals in the presence of free phosphoric acid has often been made in this laboratory with satisfaction. Favorable conditions will be found in the example which appears here: Dilution of solution, 125 c.c.; 0.2452 gram of metallic copper and 0.1827 gram of

metallic cadmium; 20 c.c. of disodium hydrogen phosphate, sp. gr. 1.0353, and 10 c.c. of phosphoric acid, sp. gr. 1.347; temperature, 60°; $N.D_{100} = 0.07-0.08$ ampere and 2.5 volts; time, 3 hours (Am. Ch. Jr., 12, 329).

7. **From Calcium.** See the separation of copper from barium, p. 124.

8. **From Chromium.** See copper from aluminium, p. 121, for the conditions of separation when the metals are present in nitric or sulphuric acid solution.

(a) *In phosphoric acid solution.* Volume of solution (containing 0.1239 gram of metallic copper and 0.1403 gram of metallic chromium as sulphates) 225 c.c., 60 c.c. of disodium hydrogen phosphate (sp. gr. 1.033) and 8 c.c. of phosphoric acid (sp. gr. 1.347); $N.D_{100} = 0.062$ ampere and 2.5 volts; temperature, 65°; time, 6 hours (J. Am. Ch. S., 21, 1003).

9. **From Cobalt:—**

(a) In the presence of nitric or sulphuric acid the separation of these two metals may be accomplished by observing the conditions given for the separation of copper from aluminium in the presence of the same acids (see p. 121). Dr. Wolcott Gibbs employed mineral acid solutions for this purpose many years ago (Z. f. a. Ch., 3, 334). Most analysts prefer the sulphate solution. Neumann is of this number. He dissolves, for example, 1 gram each of copper sulphate and cobalt sulphate in the requisite volume of water, adds 3 c.c. of concentrated sulphuric acid, dilutes to 150 c.c., and electrolyzes with $N.D_{100} = 1$ ampere at the ordinary temperature. The time required for the complete precipitation of the copper varies from $2\frac{1}{2}$ –3 hours. The filtrate or solution

poured off from the deposit of copper need only be mixed with an excess of ammonia water and then be exposed to a stronger current in order to precipitate the cobalt.

(b) *In oxalic acid solution.* The double oxalates have also been used. The method requires a strict adherence to the prescribed voltage (1.1–1.3) to yield a satisfactory result. Classen, with whom the method originated, advises the addition of 6 grams of ammonium oxalate to the solution of the salts and acidulates the liquid with oxalic acid, acetic acid, or tartaric acid. Four hours are required for the precipitation of 0.25 gram of copper (*Z. f. Elektrochem.*, 1, 291, 292; *Ber.*, 27, 2060).

(c) *In phosphoric acid solution.* An example will afford an idea of the method of procedure: Total dilution, 225 c.c.; 60 c.c. of sodium hydrogen phosphate (sp. gr. 1.033); 10 c.c. of phosphoric acid (sp. gr. 1.347); $N.D_{100} = 0.035$ ampere and 1.5 volts; temperature, 62°; time, 6 hours. Copper present, 0.1239 gram; cobalt present, 0.1000 gram. Copper found, 0.1243 gram (*J. Am. Ch. S.*, 21, 1003; *Am. Ch. Jr.*, 12, 329; *Jr. An. Ch.*, 5, 133).

10. From Gold. See p. 175.

11. From Iron:—

(a) *In nitric acid solution.* The conditions given for the separation of copper from aluminium (p. 121) will answer here. When much iron is present, difficulties will be encountered. The copper tends to redissolve (*Schweder, Berg-Hütt. Z.*, 36, 5, 11, 31).

(b) *In sulphuric acid solution.* Experience has demonstrated that the separation of the metals in question is best and most accurately made in the presence

of free sulphuric acid, observing the conditions as described on p. 121 for copper from aluminium. When the copper has been fully precipitated, which usually requires $2\frac{1}{2}$ hours, the residual solution is poured off, the copper is washed, and the liquid reduced to a suitable volume, neutralized with ammonia, and 4–6 grams of ammonium oxalate introduced into the liquid, which is then electrolyzed at 30° – 40° with a current of $N.D_{100} = 1$ – 1.5 amperes and 3.4–3.8 volts. The iron will be fully precipitated in 3–4 hours (Clas-sen, Neumann).

- (c) *In phosphoric acid solution.* In this laboratory suc-cess has attended the use of the phosphates in the presence of free phosphoric acid. Recently the proper conditions as to current density and voltage have been carefully determined. It will be seen from the appended example that the results are most satisfac-tory: Total dilution, 225 c.c.; disodium hydrogen phosphate, 60 c.c. (sp. gr. 1.0358); 10 c.c. of phos-phoric acid (sp. gr. 1.347); temperature, 53° C.; $N.D_{100} = 0.04$ ampere and 2.4 volts; time, 7 hours. Copper present, 0.1239 gram; found, 0.1237 gram (Am. Ch. Jr., 12, 329; Jr. An. Ch., 5, 133; J. Am. Ch. S., 21, 1002).
- (d) *In ammoniacal solution.* In such a solution Vort-mann separates the copper from a large quantity of iron. The liquid containing the two metals is mixed with ammonium sulphate and an excess of ammonia water. The author maintains that the ferric hy-droxide, which is of course precipitated, does not in-terfere with the deposition of the copper. The latter is free from iron. The current employed in this separation should be $N.D_{100} = 0.1$ – 0.6 ampere (M. f. Ch., 14, 552).

It is doubtful whether the copper is really free from iron. The opinion presented under the separation of nickel from iron (p. 186) and the experiences there recorded certainly make this recommendation very questionable. Indeed, in this laboratory it was found in separating the copper from iron in chalcopyrite by this method that if the precipitation of the former took place in a platinum dish it was invariably contaminated with iron. On the other hand, if the solution of metals was placed in a beaker-glass and a vertical platinum plate was made the cathode, then the copper deposited was free from iron. The ferric hydrate floating about in the platinum dish and in immediate contact with the precipitate is partially reduced to the metallic form.

(e) *In oxalic acid solution.* This procedure is due to Classen (Ber., 27, 2060), who adds to the solution containing both metals in the form of sulphates from 6–8 grams of ammonium oxalate and sufficient oxalic, acetic, or tartaric acid to render the liquid acid. The total dilution is 150 c.c. $N.D_{100} = 1$ ampere; voltage, 2.9–3.4 at 50°–60°. Time, 3 hours. It is absolutely necessary to replace the oxalic acid as it is decomposed, otherwise iron will separate upon the copper. The method requires the strictest attention to details, otherwise its results will be far from satisfactory. Indeed, its omission from the last edition of Classen's "Quantitative Electrolysis" would seem to indicate that its author had lost faith in its efficacy.

12. From Lead. The separation of these two metals has great value from the technical standpoint. It is fortunate, therefore, while both separate under the

influence of the current in a nitric acid solution, that they are deposited at opposite poles. Very considerable attention has been paid to the conditions which ought to prevail during the deposition. Many writers have contributed their experience on this point, and from them is gathered the following: The liquid electrolyzed should equal 150 c.c. in volume. It should contain 15 c.c. of nitric acid and be heated to about 60° and acted upon with a current of $N.D_{100} = 1-1.5$ amperes and 1.4 volts. In the course of an hour all the lead will have been precipitated upon the anode,—which in this separation should be a dish with roughened surface,—but not all of the copper will have been deposited on the cathode—a smaller, perforated dish. It will be noticed in the course of the decomposition that the lead separates first and the copper more slowly. When the lead is fully precipitated, wash without interrupting the current, proceed further as directed on p. 79, and after placing the liquid and wash water reduced to 130 c.c. into another weighed dish, make the latter the cathode and suspend in it the smaller dish upon which some copper had been deposited, making it the anode. The solution will give up its copper on passing the current and the metal will be deposited on the larger vessel (the cathode). It may be well to add that the liquid poured from off the lead dioxide will be quite acid, therefore neutralize it with ammonia water and add 10 c.c. of nitric acid. The electrolysis can then be conducted with $N.D_{100} = 1$ ampere and 2.2–2.5 volts, at the ordinary temperature.

- 13. From Magnesium.** See the separation of copper from barium, etc., p. 124.

14. From Manganese:—

- (a) *In sulphuric acid solution.* It should be remembered that from such a solution the manganese will be deposited upon the anode as peroxide (see p. 96); therefore, in the electrolysis let the larger dish, with rough inner surface, be made the anode to receive the manganese. The solution containing the two metals is diluted to 130–150 c.c. with the addition of 10 drops of concentrated sulphuric acid. Let the current be $N.D_{100} = 0.5\text{--}1.0$ ampere. The most favorable temperature is $50^{\circ}\text{--}60^{\circ}$. The time required is usually 2–3 hours. Experience has taught that too much manganese must not be present. When the deposition is finished, treat the deposit as already described on p. 96. The washing should be performed without interrupting the current.
- (b) *In nitric acid solution.* The separation can also be effected in the presence of free nitric acid. If the content of the latter, however, exceeds 3 to 4 per cent., instead of having the manganese precipitated on the anode it remains in solution and a red color appears at the anode due to permanganic acid. In the actual analysis, the solution of the two metals ought to be acidulated with a few cubic centimeters of acid and then electrolyzed at 60° with the same current conditions as given in *a*.

It will be wise here to observe the statement made upon page 96 as to the influence of the strong mineral acids. Indeed, if this be true, then the preceding separations are worthless and should be discarded, as has been done with the separation in oxalate solutions. In the writer's personal experience the separation in sulphuric acid solution does give satisfac-

tory results. The subject deserves further investigation.

- (c) *In phosphoric acid solution.* When free phosphoric acid is present in the solution containing salts of these metals, no question need arise as to the result, for oft-repeated tests, made in this laboratory, have amply demonstrated the accuracy of the procedure. The appended example will illustrate: $N.D_{100} = 0.05$ ampere; voltage = 2.5; temperature, 56° ; time, 6 hours; dilution, 225 c.c.; copper present, 0.1239 gram; copper found, 0.1236 gram; manganese present, 0.1200 gram; 60 c.c. of disodium hydrogen phosphate (sp. gr. 1.038); 10 c.c. of phosphoric acid (sp. gr. 1.347) (J. Am. Ch. S., 21, 1004, and Am. Ch. Jr., 12, 329).

The copper deposit in this, as well as in the many other trials conducted under practically the same conditions, was deep red in color and very adherent. It contained no manganese. The latter does not even appear at the anode, except as an amethyst color, indicating the formation there of permanganic acid.

15. **From Mercury.** See the separation of mercury from copper, pp. 150, 151.
16. **From Molybdenum.** Add 1.5 grams of pure potassium cyanide to the solution of the two metals; dilute with water to 150 c.c., heat to 60° , and electrolyze with $N.D_{100} = 0.28$ ampere and 4 volts. The copper will be completely precipitated in 5–6 hours.
17. **From Nickel:—**
- (a) *In acid solution.* This separation may be realized by observing the conditions given for the separation of copper from aluminium (p. 121) or those noted

under copper from cobalt (p. 126). That is, in nitric or sulphuric acid solution (Wolcott Gibbs, *Z. f. a. Ch.*, **3**, 334), the separation is all that the analyst can ask. The separation in oxalate solution, as recommended by Classen (*Z. f. Elektrochem.*, **1**, 291, 292), must also be executed with conditions analogous to those indicated for copper from cobalt, *b* (p. 127).

(b) *In phosphoric acid solution.* The writer has found that in the presence of free phosphoric acid this separation can be made with ease and the confidence of securing a favorable result: copper present, 0.1239 gram; copper found, 0.1241 gram; nickel present, 0.1366 gram; 60 c.c. of disodium hydrogen phosphate, sp. gr. 1.033; 10 c.c. of phosphoric acid, sp. gr. 1.347; total dilution, 225 c.c.; $N.D_{100} = 0.035$ ampere; tension = 1.5 volts; time, 6 hours; temperature, 62° C. (*J. Am. Ch. S.*, **21**, 1003). For the conditions when iron, cobalt, zinc, and copper are present together in phosphoric acid solution, see *J. Am. Ch. S.*, **21**, 1004.

18. From Palladium. See the following separation:

19. From Platinum. Add 1.5 grams of pure potassium cyanide and 5 grams of ammonium carbonate to the solution of the two metals, dilute with water to 125 c.c., heat to 70°, and electrolyze with $N.D_{100} = 0.2$ ampere and 2–2.5 volts. The copper will be precipitated in 6 hours.

20. From Potassium. See copper from barium, etc. (p. 124).

21. From Selenium. This separation has not been worked out.

22. From Sodium. See copper from barium, p. 124.

23. From Strontium. See copper from barium, p. 124.

24. From Silver. See silver from copper, p. 171. Classen proposed to precipitate the two metals with ammonium oxalate, silver oxalate being insoluble in an excess of the precipitant, while the copper salt was soluble. The former was to be filtered off, dissolved in potassium cyanide, and electrolyzed, while the filtrate containing the copper was to be subjected to a separate electrolysis. This is really not an electrolytic separation, as was shown by others (J. Am. Ch. S., 16, 420). Further, the copper deposits were invariably found to contain silver, so that it is best not to follow this procedure.

25. From Tellurium:—

In nitric acid solution. For several years, at intervals, experiments have been made in this laboratory by D. L. Wallace, upon the electrolytic separation of these metals. The results have been uniformly good with the following conditions: Copper, in grams, 0.1543; tellurium, in grams, 0.1101; dilution, 100 c.c.; 0.5 c.c. nitric acid (sp. gr. 1.42); $N.D_{100} = 0.10$ ampere and 2.06 volts; temperature, 66°–70°; time, 5 hours. Copper found: (a) 0.1541 gram; (b) 0.1546 gram; (c) 0.1543 gram; (d) 0.1542 gram.

26. From Thallium. No attempt has been made to effect this separation.

27. From Tin. Schmucker demonstrated (J. Am. Ch. S., 15, 195) that, having tin in its highest oxidation form, it is possible to precipitate and separate copper from it by adding to the solution 8 grams of tartaric acid and 30 c.c. of ammonia water (sp. gr. 0.91), then electrolyzing at 50° C. with $N.D_{100} = 0.04$ ampere and 1.8 volts. If a tenth of a gram of each metal be present, the copper will be precipitated in 5 hours. The total dilution was 175 c.c.

As observed in preceding paragraphs, this method was utilized by Schmucker in the separation of copper from arsenic and copper from antimony. The same author also separated copper from a mixture of antimony, arsenic, and tin, using the conditions as described above.

Or, when antimony, arsenic, and tin are associated with copper, treat the four sulphides with sodium sulphide. The resulting alkaline sulphide solution can then be employed for the separation of the first three (p. 177), while the insoluble copper sulphide may be dissolved and treated as described on p. 65.

28. From Tungsten. The conditions given for the separation of copper from molybdenum (p. 132) may be used for this separation.

29. From Uranium:—

(a) *In nitric acid solution.* Add 0.5 c.c. of concentrated nitric acid to the solution, dilute to 150 c.c., heat to 60°, and electrolyze with $N.D_{100} = 0.14-0.27$ ampere and 2-2.4 volts. The copper will be precipitated in 3 hours.

(b) *In sulphuric acid solution.* The solution of these metals should be mixed with 2 c.c. of concentrated sulphuric acid, diluted to 150 c.c. with water, heated to 50°-60°, and electrolyzed with $N.D_{100} = 0.16$ ampere and 2 volts. The precipitation will be complete in 4 hours.

30. From Vanadium. A method of separation is lacking.

31. From Zinc:—

(a) *In nitric acid solution.* The conditions mentioned under *a* in copper from aluminium (p. 121), and under copper from cobalt (p. 126) and nickel (p. 132), will answer here in getting a satisfactory separation.

The solution must be kept acid during the decomposition. To this may be added, that to a solution containing 0.1341 gram of copper and equal amounts of zinc, cobalt, and nickel, 5 c.c. of nitric acid were added, the liquid was diluted to 200 c.c., and electrolyzed with 0.04 ampere, when 0.1339 gram of copper was obtained.

- (b) *In sulphuric acid solution.* The conditions are analogous to those employed for the separation of copper from aluminium (p. 121), cobalt (p. 126), and nickel (p. 132).
- (c) *In oxalate solution.* This method (Ber., 17, 2467) is no longer recommended. Only the most careful observance of the conditions given will yield anything like a satisfactory result.
- (d) *In phosphoric acid solution* (Am. Ch. Jr., 12, 329; Jr. An. Ch., 5, 133). The early suggestions that these metals be precipitated as phosphates and the latter be then dissolved in phosphoric acid and the resulting solution be electrolyzed were not favorably received. Here, in this laboratory, where the separation had been repeatedly performed, the method gave satisfaction. To extend its application the most favorable conditions have been worked out and repeated. They are given in the example which follows:—

To the solution of the sulphates, containing 0.1239 gram of copper and a like quantity of zinc, were added 60 c.c. of disodium hydrogen phosphate (sp. gr. 1.033) and 10 c.c. of phosphoric acid (sp. gr. 1.347). It was diluted to 225 c.c., heated to 60°, and electrolyzed with $N.D_{100} = 0.035$ ampere and 2.5 volts, for 5 hours, when 0.1244 gram of copper was obtained, free from zinc.

Another interesting separation, properly belonging here, was that of copper from a mixture of iron, cobalt, and zinc. The solution diluted to 225 c.c. contained:—

0.1239 gram of copper
0.1007 “ “ cobalt
0.1000 “ “ iron
0.1200 “ “ zinc
30 c.c. of Na_2HPO_4 (sp. gr. 1.0358)
15 “ “ H_3PO_4 (sp. gr. 1.347)

It was electrolyzed at 57° with a current of $\text{N.D.}_{100} = 0.04\text{--}0.05$ ampere and 2.3 volts. In six hours the copper was fully precipitated. It weighed 0.1240 gram and contained none of the other metals (J. Am. Ch. S., 21, 1003, 1004).

CADMIUM.

The ordinary gravimetric methods for the determination of this metal are such that they can frequently with advantage be replaced by the electrolytic process. The same is true when it comes to the separation of cadmium from the metals usually associated with it, as well as those with which it only occasionally occurs. The writer prefers the electrolytic course whenever it is available. To what extent the various suggestions offered for the electrolytic determination of the metal can be applied in separations may be gathered from the following paragraphs:—

1. From Aluminium:—

(a) *In sulphuric acid solution.* In this separation it is only necessary to add to the solution of the salts of the

metals 3 c.c. of sulphuric acid, of specific gravity 1.09, dilute to 125 c.c. with water, heat to 65°, and electrolyze with $N.D_{100} = 0.078$ ampere and 2.61 volts. The cadmium will be deposited in the course of from 4–4½ hours. It should be washed without interrupting the current. In one case 0.1111 Cd instead of 0.1105 was found; in another, 0.1181 instead of 0.1188 gram; and in a third, 0.1604 instead of 0.1599 gram.

- (b) *In phosphoric acid solution.* Add an excess of disodium hydrogen phosphate (sp. gr. 1.0358) to the solution of the metals and then sufficient phosphoric acid (sp. gr. 1.347) to leave about 1.5 c.c. of the latter in excess. Dilute with water to 100 c.c., heat to 50°, and electrolyze with $N.D_{100} = 0.06$ ampere and 3 volts. Time, 7 hours. See p. 69 for further details. (J. Am. Ch. S., 20, 279; Am. Ch. Jr., 12, 329; 13, 206).

2. **From Antimony.** Schmucker (J. Am. Ch. S., 15, 195) used for this purpose the method described on p. 121 for the separation of copper from antimony, observing the same conditions. The results were perfectly satisfactory. In washing the cadmium deposit water alone was used. The deposition was made during the night, but by heating the electrolyte the time factor can be much reduced.

3. **From Arsenic:—**

- (a) *In ammoniacal tartrate solution.* Proceed precisely as directed on p. 123 in the separation of copper from arsenic (J. Am. Ch. S., 15, 195).
- (b) *In alkaline cyanide solution.* After converting the arsenic into its highest state of oxidation, add from 2 to 3 grams of potassium cyanide to the solution containing the metals and electrolyze with a

pressure not exceeding 2.6 volts (Am. Ch. Jr., 12, 428; Z. f. ph. Ch., 12, 122).

4. **From Barium, Strontium, Calcium, Magnesium, and the Alkali Metals.** No records of any such separations have been made.
5. **From Beryllium.** There is no record of this separation.
6. **From Bismuth.** See separation of bismuth from cadmium, p. 157.
7. **From Chromium.** The conditions given for the separation of cadmium from aluminium will answer equally well in this case.
8. **From Cobalt:—**
 - (a) *In sulphuric acid solution.* Use the conditions prescribed for the separation of cadmium from aluminium (p. 137). It may be well to add that the addition of ammonium sulphate to the solution is advantageous. The voltage should not exceed 2.8–2.9.
 - (b) *In alkaline cyanide solution.* Add 4–5 grams of pure potassium cyanide to the solution of the metals, dilute to 200 c.c., and electrolyze with $N.D_{100} = 0.3$ ampere and 2.6 volts (Am. Ch. Jr., 12, 104; Z. f. ph. Ch., 12, 116).
9. **From Copper.** See also copper from cadmium, pp. 124, 125. In addition to the methods used in separating these metals, in which the copper is precipitated, we may add the following: Introduce 5 to 6 grams of pure potassium cyanide into the solution of the metals for every 0.2–0.4 gram of cadmium and copper. Dilute the solution to 200 c.c. and electrolyze with a current of $N.D_{100} = 0.02$ – 0.04 ampere and 2.6–2.7 volts. The cadmium will be deposited; the copper will remain dissolved (Jr. An. Ch., 3, 385; Z. f. ph. Ch., 12, 122). Rimbach (Z. f. a. Ch., 37,

288) has tried this separation with marked success in the analysis of aluminium-cadmium-tin alloys containing copper as impurity. In case the nitrate of cadmium is used it will be necessary to increase the current to $N.D_{100} = 0.4$ ampere.

10. From Gold. This separation is not recorded. It is probable that it can be executed in a hot alkaline cyanide solution.

11. From Iron:—

(a) *In sulphuric acid solution.* Follow the directions given in *a* under cadmium from aluminium, p. 137. It may be observed that this is the procedure used, too, in separating cadmium from chromium.

(b) *In phosphoric acid solution.* Again the conditions noticed in *b* under cadmium from aluminium (p. 138) will prove to be very satisfactory in this particular case.

(c) *In potassium cyanide solution.* Dissolve a mixture of cadmium and ferrous sulphates in 100 c.c. of water, previously acidulated with a few drops of dilute sulphuric acid, introduce 2 to 3 grams of pure potassium cyanide, and heat gently until perfect solution ensues. If considerable time elapses before the liquid becomes yellow in color, add a few drops of caustic potash. Dilute the liquid to 200 c.c. and electrolyze the cold solution with a current of $N.D_{100} = 0.05-0.1$ ampere. The deposit of cadmium will be very satisfactory (W. Stortenbeker, *Z. f. Elektrochem.*, 4, 409).

12. From Lead. See lead from cadmium, p. 165.

13. From Magnesium. See cadmium from barium, etc., p. 139. In this connection it may be stated that Rimbach (*Z. f. a. Ch.*, 37, 289) effected this separation in a

potassium cyanide solution. The precaution is made that not too much magnesia be present, ammonium chloride also being added to the solution to hold up the magnesia. The current strength best adapted for this separation proved to be $N.D_{100} = 0.02-0.05$ ampere. The time was 14 hours.

14. From Manganese:—

(a) *In sulphuric acid solution.* As manganese separates readily from a sulphate solution in the presence of a slight excess of sulphuric acid, and then, too, upon the anode (p. 95), it is only necessary to add from 2 to 3 c.c. of sulphuric acid (sp. gr. 1.09) to the solution of the metals, dilute to 125 c.c., and electrolyze with the current and voltage given under cadmium from aluminium, *a*. As the manganese is precipitated upon the anode as dioxide, make the larger dish the receiving vessel for it; further, let its inner surface be roughened. The cadmium is deposited upon the cathode. The method has been used in this laboratory with success.

(b) *In phosphoric acid solution.* An idea of the accuracy of the method can be best obtained from an actual example. The conditions also for work will be most satisfactorily learned from it. Twenty cubic centimetres of disodium hydrogen phosphate (sp. gr. 1.0358) and 3 c.c. of phosphoric acid (sp. gr. 1.347) were added to a solution containing 0.2399 gram of cadmium and 0.1000 gram of manganese and the liquid then diluted with water to 150 c.c. and electrolyzed at the ordinary temperature with a current of 1 ampere. In 12 hours 0.2394 gram of cadmium was precipitated. There was not the slightest deposition of manganese at the anode. The cadmium deposit

was crystalline in appearance. It was washed with hot water. Before the final interruption, the current ought to be increased and allowed to act for an hour. The acid liquid should be removed with a siphon before disconnecting (Am. Ch. Jr., 13, 206).

15. **From Mercury.** See mercury from cadmium, p. 149.

16. **From Molybdenum.** The alkaline cyanide solution is well adapted for this purpose. Add from 1.5 to 3 grams of pure potassium cyanide, dilute to 200 c.c., and electrolyze at 40° C. with $N.D_{100} = 0.03-0.04$ ampere and 2.25-3.0 volts. The conditions are practically those used in the separation of cadmium from arsenic (Am. Ch. Jr., 12, 428).

17. **From Nickel:—**

(a) *In sulphuric acid solution.* To the solution of salts of the two metals add 2 to 3 c.c. of sulphuric acid, sp. gr. 1.09, also ammonium sulphate, and electrolyze with the current density and voltage mentioned in the separation of cadmium from aluminium, *a*, p. 137.

(b) *In phosphoric acid solution.* 0.1827 gram of cadmium and 0.1500 gram of nickel (both as sulphates) were precipitated by 40 c.c. of disodium hydrogen phosphate, dissolved in 3 c.c. of phosphoric acid (sp. gr. 1.347), diluted to 125 c.c., and electrolyzed at the ordinary temperature with $N.D_{100} = 0.035$ ampere and 2.5-3.0 volts. The precipitated cadmium weighed 0.1820 gram. It was washed and treated as directed upon p. 69.

(c) *In alkaline cyanide solution.* The solution containing the double cyanides of the two metals is well suited for this separation, but it is absolutely necessary to have a little free sodium hydroxide present.

The conditions would be then about as follows: Add to the solution containing 0.1723 gram of cadmium, and 0.1600 gram of nickel, 2 grams of potassium or sodium hydroxide and 3 grams of potassium cyanide. Dilute to 175 c.c. and electrolyze at 40° with $N.D_{100} = 0.03-0.04$ ampere and 2.25-3.0 volts (Am. Ch. Jr., 12, 104; Freudenberg, Z. f. ph. Ch., 12, 122).

18. **From Osmium.** The only recorded separation of these two metals was made in a solution of potassium cyanide. The quantity of cyanide was 1.5 grams for 0.3 gram of the combined metals. The dilution of the solution equaled 170 c.c.; it was electrolyzed with a current of $N.D_{100} = 0.26$ ampere and 3-4 volts. Time, 10 hours; temperature, 25° (Jr. An. Ch., 6, 87).

An electrolytic separation of cadmium from platinum and palladium is not known (Am. Ch. Jr., 12, 428; 13, 417).

19. **From Selenium.** This separation has not been made.
20. **From Silver.** See p. 169, for silver from cadmium.
21. **From Sodium.** See the separation of cadmium from barium, etc., p. 139.
22. **From Strontium.** See the separation of cadmium from barium, etc., p. 139.
23. **From Tellurium.** There is no known electrolytic separation.
24. **From Tin.** They have not been separated electrolytically.
25. **From Tungsten.** The conditions detailed in the separation of cadmium from arsenic (p. 138) and under cadmium from molybdenum (p. 142) in cyanide solution will answer here.
26. **From Uranium.** The current has not been used in their separation.

27. From Vanadium. They have not been separated in the electrolytic way.

28. From Zinc. As these two metals are so frequently found together, both in natural and in artificial products, it is not surprising that electrolytic methods have been sought to effect their separation in such a manner as to leave no doubt in the mind of the analyst. They should be and indeed are preferable to the ordinary gravimetric procedures.

The first method proposed and published was that by Yver (B. s. Ch. Paris, 34, 18). It is based upon the fact that cadmium separates well—

(a) *In acetate solutions.* Convert the metals into acetates by the addition of 2 to 3 grams of sodium acetate to their solution, followed by several drops of free acetic acid. Dilute the liquid to 100 c.c. and warm to 70° C. Electrolyze with $N.D_{100} = 0.10$ ampere and 2.2 volts. Time, 3–4 hours. The cadmium (0.2 gram) will be precipitated in a crystalline form and free from zinc (Am. Ch. Jr., 8, 210).

The zinc in the liquid from the cadmium deposit may then be precipitated by the method of Richè (p. 89).

Mention may be here made of the fact that Smith and Knerr (Am. Ch. Jr., 8, 210) electrolyzed a solution of cadmium and zinc to which 3–4 grams of sodium tartrate and tartaric acid had been added, with a current of $N.D_{100} = 0.3-0.4$ ampere and 2.25–3 volts. The temperature of the solution was 60°.

(b) *In oxalic acid solution.* Eliasberg (Z. f. a. Ch., 24, 550) proposed this method, second in point of time, and recommended the following procedure: Dissolve the metallic oxides in hydrochloric acid, evaporate

their solution to dryness, take up the residue in water, add to the liquid 8 grams of potassium oxalate ($\text{C}_2\text{O}_4\text{K}_2$) and 2 grams of ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$), dilute to 120 c.c., heat to 80° – 85° , and electrolyze with $\text{N.D}_{100} = 0.01$ – 0.02 ampere and 3 volts. The cadmium will be precipitated free from zinc. See also Waller, Z. f. Elektrochem., 4, 241–247. From 6 to 7 hours are required for the deposition of 0.2 gram of cadmium.

- (c) *In sulphuric acid solution.* To the liquid containing the salts of the two metals add 3 to 4 c.c. of a concentrated ammonium sulphate solution and follow with 2 to 3 c.c. of dilute sulphuric acid. Dilute to 100 c.c. and electrolyze with $\text{N.D}_{100} = 0.08$ ampere and 2.8–2.9 volts (Neumann's *Elektrolyse*, p. 189).

In the electro-chemical laboratory of the University of Munich the separation of cadmium from zinc is in a certain sense a combination of *c* and *a*. For example, sodium hydroxide is added to the sulphates of the metals until a permanent precipitate is formed; this is then dissolved in as little sulphuric acid as possible, the solution is diluted to 70 c.c. and the cadmium precipitated by a current of $\text{N.D}_{100} = 0.07$ ampere. When the greater portion of this metal has been thrown out of the solution, the free sulphuric acid is neutralized with sodium hydroxide and 2 to 3 grams of sodium acetate are introduced into the liquid, which is heated to 45° and electrolyzed with a current of $\text{N.D}_{100} = 0.03$ ampere and 3.6 volts.

- (d) *In phosphoric acid solution.* Total dilution, 125 c.c.; cadmium, 0.1827 gram; zinc, 0.1500 gram; disodium hydrogen phosphate (sp. gr. 1.038), 40 c.c.; phosphoric acid (sp. gr. 1.347), 3 c.c.; $\text{N.D}_{100} = 0.035$

ampere; $V = 2.5-3.0$. Cadmium found, 0.1820 gram. The ordinary temperature. Time, 10 hours (Am. Ch. Jr., 12, 329).

- (e) *In potassium cyanide solution.* This separation originated in this laboratory (Am. Ch. Jr., 11, 352). Example: 0.2426 gram of cadmium as sulphate, 0.2000 gram of zinc as sulphate; 4.5 grams of potassium cyanide; total dilution, 200 c.c. Ordinary temperature. $N.D_{100} = 0.03$ ampere; volts = 2.8–3.2. 0.2429 gram of cadmium found.

In the filtrate the zinc may be precipitated by increasing the current. Freudenberg used this method with success, applying a current corresponding to an electromotive force of 2.6–2.7 volts.

MERCURY.

Experience has proved that this metal is most accurately determined, and most satisfactorily separated from the metals usually found with it by the use of electrolytic methods which in this instance are preferable in every particular to the ordinary gravimetric courses; hence all the known separations in the electrolytic way will be given, in the paragraphs which follow, with such detail that no doubt need remain as to the final results.

1. From Aluminium:—

- (a) *In nitric acid solution* (p. 121). Add 3 c.c. of concentrated nitric acid to the solution of the two salts, dilute to 125 c.c., heat to 70° C., and electrolyze with $N.D_{100} = 0.06$ ampere and 2 volts. Time, 2 hours. The solution in the dish must be siphoned off before the interruption of the current.
- (b) *In sulphuric acid solution* (p. 121). Add 1 c.c. of

sulphuric acid to the solution of the salts; dilute to 125 c.c.; heat to 65° and electrolyze with $N.D_{100} = 0.4-0.6$ ampere and 3.50 volts. The mercury (0.1500 gram) will be precipitated in an hour. Wash it with cold water and proceed as directed on p. 74.

2. **From Antimony.** Add to the solution, containing about equal amounts of the two metals, 5 grams of tartaric acid and 15–20 c.c. of ammonia water (10 per cent.); dilute to 175 c.c. and electrolyze with $N.D_{100} = 0.015-0.085$ ampere and 2.2–3.5 volts. The temperature should be 50°. About 6 hours will be required for the precipitation (J. Am. Ch. S., 15, 205). The antimony must exist in solution as an antimonious compound. The method was first worked out by Schmucker (*loc. cit.*) and was later successfully confirmed by Freudenberg in his study of the differences in potential (Z. f. ph. Ch., 12, 112), when he employed an electromotive force of 1.6–1.7 volts. Mercury used, 0.2362 gram; mercury found, 0.2356 gram; antimony present, 0.2600 gram.

The liquid from the deposit of mercury, after acidulation, may be precipitated with hydrogen sulphide and the resulting sulphide be dissolved in sodium sulphide and treated as described on p. 115 for the determination of the antimony.

3. **From Arsenic:—**

(a) *In nitric acid solution.* The solution of the metals should contain a few cubic centimetres of free nitric acid and then be acted upon with an electromotive force of 1.7–1.8 volts: Mercury taken, 0.2380 gram; mercury found, 0.2380 gram; arsenic present, 0.2516 gram (Freudenberg, Z. f. ph. Ch., 12, 111).

(b) *In potassium cyanide solution.* Add 3 grams of

pure potassium cyanide to the liquid containing 0.5 gram of combined metals, dilute to 200 c.c., and electrolyze with $N.D_{100} = 0.015$ ampere and 2.2–3.5 volts for 5 hours at 65° (Am. Ch. Jr., 12, 428). It is immaterial whether the arsenic is present as an arsenite or arsenate.

(c) *In alkaline sulphide solution* (p. 74). An example will best illustrate the method: To the solution of mercury add 25 c.c. of sodium sulphide (sp. gr. 1.19), dilute with water to 125 c.c., heat to 70° C., and electrolyze with a current of $N.D_{100} = 0.11$ ampere and 2.5 volts. The time for precipitation is usually 5 hours. See Jr. Fr. Ins., 1891.

4. **From Barium, Strontium, Calcium, Magnesium, and the Alkali Metals.** Use method *a* under mercury from aluminium (p. 146) for this purpose.

5. **From Bismuth.** The statements with reference to the separation of these two metals are contradictory. The experiments conducted in this laboratory (Jr. An. Ch., 7, 252) showed that the metals were coprecipitated from a nitric acid solution, as one from many examples will illustrate: The solution contained 0.1132 gram of mercury and 0.0716 gram of bismuth. Ten cubic centimetres of nitric acid of specific gravity 1.2 were added and the liquid diluted with water to 200 c.c. and electrolyzed with a current of $N.D_{100} = 0.04$ ampere and 1.6 volts.

The precipitation of the metals was complete, but the mercury contained bismuth. This was one of eight trials which resulted similarly. They were made to disprove a statement which had appeared repeatedly in three editions of Classen's *Quantitative Analyse durch Elektrolyse* (p. 147, 2d ed.), despite the fact that the

same writer had declared previously (Ber., 19, 325): "Bismuth cannot be separated from mercury in this manner. Both metals are precipitated simultaneously from an acid solution."

After this study had been made, Freudenberg (Z. f. ph. Ch., 12, 111), by adherence to the idea of the differences in potential, gave results which would indicate a complete separation; a few cubic centimetres of nitric acid, of sp. gr. 1.2, and 2-4 grams of ammonium nitrate are added to the nitrate solution of the two metals and the electrolysis conducted with a potential of 1.3 volts. Mercury used, 0.2380 gram; mercury found, 0.2376 gram; bismuth present, 0.2694 gram. As Neumann (*Elektrolyse*, p. 181) remarks, the possible current strength is exceedingly low, hence a long time is required for the precipitation of the mercury.

While the writer has never tested the recommendation of Freudenberg, his experience gathered from numerous attempts on the part of his students inclines him to say that the procedure is worthy of further study at least.

6. From Cadmium:—

(a) *In acid solution.* The nitric acid and sulphuric acid solutions lend themselves quite well to this separation. The proper conditions for the obtaining of satisfactory results are given in the section on mercury from aluminium, paragraphs *a* and *b* (p. 146).

(b) *In alkaline cyanide solution.* The solution contained 0.1182 gram of mercury and 0.2206 gram of cadmium. Two and one-half grams of pure potassium cyanide were added, and the liquid was then diluted with water to 125 c.c., heated to 65°,

and acted upon with a current of $N.D_{100} = 0.018$ ampere and 1.7 volts. The precipitation was complete in 7 hours at the ordinary temperature (J. Am. Ch. S., 21, 919; also 17, 612).

7. **From Calcium.** See the separation of mercury from barium (p. 148).
8. **From Chromium.** The methods recommended for the separation of mercury from aluminium, pp. 146, 147, will answer for this particular purpose.
9. **From Cobalt:—**
 - (a) *In acid solutions.* See p. 146, under mercury from aluminium.
 - (b) *In alkaline cyanide solution.* The solution contained 0.1216 gram of mercury and 0.1000 gram of cobalt. The liquid was diluted to 100 c.c.; 2 grams of potassium cyanide were added to it and the liquid, then heated to 65°, was electrolyzed with $N.D_{100} = 0.025-0.03$ ampere and 2.06–2.7 volts for 5 hours. The mercury found equaled 0.1213 gram and 0.1217 gram. Too much potassium cyanide exercises a retarding influence on the precipitation of the mercury (J. Am. Ch. S., 21, 918; Am. Ch. Jr., 12, 104).
10. **From Copper:—**
 - (a) *In nitric acid solution.* Freudenberg (Z. f. ph. Ch., 12, 111), with attention to voltage alone, separates these metals as follows: To their solution (the nitrates) add several cubic centimetres of nitric acid (sp. gr. 1.2) and 2 to 4 grams of ammonium nitrate, after which electrolyze with a current having a pressure of 1.3 volts. Mercury present, 0.2380 gram; copper present, 0.1356 gram; mercury found, 0.2377 gram; copper found, 0.1358 gram. The separation was made during the night.

(b) *In alkaline cyanide solution.* It was in a solution of the double cyanides of these metals that they were first separated successfully in the electrolytic way (Am. Ch. Jr., 11, 264). At the time it was thought that the separation could not be regarded as yielding trustworthy results when the copper exceeded 20 per cent., but about two years subsequently it was shown (Jr. An. Ch., 5, 489) that by careful adjustment of the current strength the quantity of copper could not only equal, but exceed, that of the mercury almost indefinitely (Spare and Smith, J. Am. Ch. S., 23, 579). The time, however, was still an important factor, and it was not reduced by Freudenberg, who electrolyzed the double cyanides with a pressure of 2.5 volts, in the presence of 2 to 4 grams of potassium cyanide (Z. f. ph. Ch., 12, 113). The reduction of this factor was made in 1894 (J. Am. Ch. S., 16, 42) by gently warming the electrolyte. It then became possible to fully precipitate the mercury in three and one-half hours. Since then the separation has been repeatedly made both with mercury and copper (J. Am. Ch. S., 21, 917), and with mercury, copper, cadmium, zinc, and nickel simultaneously present. The following conditions will prove satisfactory for this separation: Mercury present, 0.1216 gram; copper present, equal amount; total dilution, 125 c.c.; potassium cyanide, 2-3 grams; temperature, 65°; time, 2½-3 hours. Mercury found, 0.1215 gram (Revay, Z. f. Elektrochem., 4, 313).

11. **From Gold.** This separation has not been made. See Z. f. ph. Ch., 12, 113.

12. **From Iron:—**

(a) *In nitric acid solution.* Use the conditions indicated under a, mercury from aluminium (p. 146).

- (b) *In sulphuric acid solution.* See *b* under mercury from aluminium.
- (c) *In alkaline cyanide solution.* Dissolve ferrous ammonium sulphate in water; conduct sulphur dioxide through it to reduce any ferric salt which may be present, nearly neutralize the excess of acid with sodium carbonate, mix with the solution of the silver salt, and add from 2.5 to 4 grams of potassium cyanide for 0.2–0.4 gram of the combined metals; then electrolyze with $N.D_{100} = 0.02-0.05$ ampere and 2.5 volts, with a temperature of 70° . The total dilution should equal 125 c.c. Time, 3–4 hours (J. Am. Ch. S., 21, 920).

13. From Lead. To the solution, containing the two metals, add from 25 to 30 c.c. of nitric acid (sp. gr. 1.3), dilute to 175 c.c. with water, and electrolyze with a current of $N.D_{100} = 0.13$ to 0.18 ampere and 2 volts, at 30° for 4 hours. It will, of course, be understood that the lead is deposited as dioxide upon the anode while the mercury is simultaneously precipitated in the cathode. Use a dish as anode (Smith and Moyer, Jr. An. Ch., 7, 252; Z. f. anorg. Ch., 4, 267; Heidenreich, Ber., 29, 1585; Z. f. Elektrochem., 3, 151).

14. From Magnesium. See the separation of mercury from barium, etc., p. 148.

15. From Manganese:—

- (a) *In nitric acid solution.* See the conditions under which manganese is precipitated as dioxide (p. 95). The mercury separates at the cathode.
- (b) *In sulphuric acid solution.* The conditions which should be observed in depositing manganese from a solution containing free sulphuric acid will answer

in this particular separation (p. 96). The larger dish must, of course, be made the anode. The quantities of the two metals must not be too large.

16. From Molybdenum. The separation is readily effected in an alkaline cyanide solution, using the conditions prescribed under *b* in the separation of mercury from arsenic (p. 147).

17. From Nickel:—

(a) *In nitric acid solution.* Follow the conditions given under *a* in the separation of mercury from aluminium, p. 146.

(b) *In sulphuric acid solution.* Reproduce the conditions of *b* in the separation of mercury from aluminium, p. 146.

(c) *In alkaline cyanide solution.* An example will illustrate: Mercury present, 0.1216 gram; nickel present, 0.1500 gram; potassium cyanide, 2–2.5 grams; total dilution, 125 c.c.; $N.D_{100} = 0.04$ ampere; volts = 1.7–2.2; temperature, 65°; time, 4 hours. The mercury found equaled 0.1213 gram (J. Am. Ch. S., 21, 918; Am. Ch. Jr., 12, 104).

18. From Osmium. Follow the directions for the separation of mercury from arsenic in an alkaline cyanide solution, p. 147. In this separation the quantity of alkaline cyanide should not exceed 1.5 grams for 0.2 gram of metal (Am. Ch. Jr., 12, 428; 13, 417; Jr. An. Ch., 6, 87).

19. From Palladium. Let the conditions be the same as those given for the separation of mercury from platinum (see below) (Am. Ch. Jr., 12, 428).

20. From Platinum. Example: Mercury present, 0.1373 gram; platinum present, 0.1000 gram; total dilution, 125 c.c.; potassium cyanide, 3 grams; $N.D_{100} = 0.04$ —

0.05 ampere; $V = 2.1$; temperature, 65° – 75° ; time, 4 hours. The mercury found equaled 0.1372 gram (Am. Ch. Jr., 13, 417; J. Am. Ch. S., 21, 920).

21. From Potassium. See mercury from barium, etc., p. 148.

22. From Silver. These metals cannot be separated electrolytically either in an acid or alkaline cyanide solution. Classen precipitates them together, and after ascertaining their combined weight expels the mercury by ignition and weighs the residual silver.

23. From Sodium. See barium, p. 148.

24. From Strontium. See mercury from calcium, etc., p. 148.

25. From Tellurium. There is no known electrolytic separation.

26. From Tin:—

(a) *In alkaline sulphide solution.* The conditions mentioned under mercury (p. 74) will answer perfectly for this separation (Jr. Fr. Ins., 1891). To change the sodium sulpho-salt in the filtrate into ammonium sulphostannate consult p. 113.

(b) *In ammoniacal tartrate solution.* A solution of the two metals was made by adding mercuric chloride to tartaric acid, followed by ammonia water and then diluting with water. This solution was then mixed with the tin salt solution and the combined liquids electrolyzed with a current showing a pressure of from 1.6–1.7 volts. (See the separation of mercury from antimony in tartrate solution, p. 147; also J. Am. Ch. S., 15, p. 204.)

It may be of interest to state that the conditions given for the separation of mercury from antimony (p. 147), and those just employed above

for the separation of mercury from tin have been successfully applied by Schmucker (J. Am. Ch. S., 15, 204) for the electrolytic separation of mercury from a solution containing arsenic, antimony, and tin, the only change being in the addition of an increased amount of tartaric acid and ammonia water. Example: Mercury, 0.0933 gram; arsenic, 0.1009 gram; antimony, 0.1031 gram; tin, 0.1000 gram; tartaric acid, 8 grams; ammonia, 30 c.c.; dilution, 175 c.c.; $N.D_{100} = 0.05$ ampere; volts = 1.7. The precipitation made at 60° was complete in 6 hours.

27. From Tungsten. Use conditions corresponding to those employed in the separation of mercury from arsenic in an alkaline cyanide solution (p. 147).

28. From Uranium. There is no recorded electrolytic separation of these metals, but it is quite probable that methods *a* and *b*, under mercury from aluminium (p. 146), would be applicable in this case.

29. From Vanadium. They have not been separated by the current.

30. From Zinc:—

(a) *In acid solutions* (nitric or sulphuric) the conditions mentioned under *a* and *b*, in the separation of mercury from aluminium, will prove perfectly satisfactory (p. 146).

(b) *In alkaline cyanide solution.* This separation has been made repeatedly with excellent success, so that perhaps an actual example will give all the data necessary to guide others in making the separation: Mercury present, 0.1158 gram; zinc present, 0.1000 gram; potassium cyanide, 1.5 to 2 grams; dilution, 125 c.c.; $N.D_{100} = 0.025-0.05$ ampere; $V = 2.5$ to 3;

time, 4 hours; temperature, 60°. Mercury found, 0.1155 gram (J. Am. Ch. S., 21, 919; Jr. Fr. Ins., 1889).

- (c) *In phosphoric acid solution.* An example from many results will show the conditions which should be pursued in conducting the separation in a solution such as just indicated: 25 c.c. of mercuric chloride = 0.1159 gram of metal; 25 c.c. of zinc sulphate = 0.1010 gram of metal; 60 c.c. of disodium hydrogen phosphate (1.038 sp. gr.); 10 c.c. of phosphoric acid (1.347 sp. gr.); total dilution, 175 c.c.; temperature, 60°; $N_{100} = 0.01$ ampere; $V = 1.5$; time, 4-5 hours. Mercury found, 0.1163 gram (J. Am. Ch. S., 21, 1006).

BISMUTH.

The separations of this metal from other metals in the electrolytic way are not numerous, but they are, notwithstanding, of decided help to the analyst, and therefore will be here presented in such detail as is known.

1. **From Aluminium.** The conditions given under bismuth for its determination in a nitric (p. 76) or sulphuric acid (p. 76) solution can be here used for its separation from aluminium. Its precipitation as an amalgam (p. 75) is well adapted for this purpose.
2. **From Antimony.** To the solution containing the two metals add 5 grams of tartaric acid, 15 c.c. of ammonium hydroxide, dilute to 175 c.c. with water, and electrolyze with a current of $N.D_{100} = 0.022$ ampere and 1.8 volts at 50° for 6 hours (J. Am. Ch. S., 15, 203).
3. **From Arsenic.** The course just outlined for the separation of bismuth from antimony will answer in this

case (J. Am. Ch. S., 15, 202). Neumann (Elektrolyse, p. 185) states that the two metals, if in sulphate solution, can be separated with a current having an *E. M. F.* of 1.9 volts.

4. **From Barium.** The conditions for the precipitation of bismuth from nitric acid solution (p. 76) will answer for this separation.
5. **From Cadmium.** This separation may be conducted in the presence of free nitric acid (p. 76), by the amalgam method (p. 75), or in a sulphuric acid solution. If using the last electrolyte, proceed as follows: Dissolve 0.1500 gram of cadmium metal in 2 c.c. of concentrated sulphuric acid (sp. gr. 1.84) and to this solution add another of 0.15 gram of bismuth and 1 c.c. of concentrated nitric acid, 1 gram of potassium sulphate, and dilute with water to 150 c.c., heat to 50°, and electrolyze with a current of $N.D_{100} = 0.025$ ampere and 2 volts. Time, 8 hours. The bismuth will be deposited in a bright, metallic form (Kammerer).
6. **From Calcium.** The conditions given on pp. 75–78 for the determination of bismuth may be relied upon in making this separation.
7. **From Chromium.** Use a nitric acid solution (p. 76), or adopt the method given in the following paragraph:—
To a solution of bismuth containing 0.1500 gram of metal and 1 c.c. of nitric acid (sp. gr. 1.42) add 0.5 gram of potassium sulphate, 2 c.c. of sulphuric acid (sp. gr. 1.84), and a quantity of chrome alum equivalent to 0.1500 gram of chromium. Dilute to 150 c.c. with water and electrolyze with a current strength of $N.D_{100} = 0.025$ ampere and 2 volts, the temperature being maintained at 50° C. After 8 hours the deposition will be complete and the bismuth will be free from chromium.

RESULTS.

BISMUTH TAKEN.	BISMUTH FOUND.	CHROMIUM.	POTASSIUM SULPHATE.	SULPHURIC ACID.	DILUTION.	TIME.	TEMPERATURE.	N.D. ₁₀₀ .	VOLTS.	STYLE OF ANODE.
Grm.	Grm.	Grm.	Grm.	C.c.	C.c.	Hours.	°C.	AMP.		
0.1434	0.1430	0.1500	0.5	2	200	9	50	0.03	2	Gauze.
0.1434	0.1428	0.150	0.5	2	150	9	50	0.025	2	Basket.
0.1434	0.1434	0.1500	0.5	2	200	8½	50	0.025	2	Gauze.
0.1434	0.1428	0.1500	0.5	2	150	8½	50	0.02	2	Basket.
0.1434	0.1430	0.1500	0.5	2	150	8½	50	0.02	2	Spiral.
0.1434	0.1429	0.1500	0.5	2	150	9	50	0.025	2	"

The chromium salt seems to exert a beneficial influence on the character of the deposit. Much of the chromium, during the electrolysis, is oxidized to chromic acid. Especially is this true when gauze electrodes are used (Kammerer).

8. **From Cobalt.** Proceed as in the separation from aluminium (p. 156), or from chromium (above).
9. **From Copper.** In a nitric acid solution copper and bismuth cannot be separated electrolytically. This statement has been the subject of considerable controversy in past years (*Z. f. anorg. Ch.*, 3, 415; 4, 234; 5, 197; 6, 43; *Z. f. ph. Ch.*, 12, 117), so that all that remains to chemists is the suggestion made in the *Am. Ch. Jr.*, 12, 428—viz., add from 3 to 4 grams of citric acid to the bismuth solution, supersaturate the latter with sodium hydroxide, and into this mixture pour the copper salt solution, containing a slight excess of potassium cyanide, and electrolyze at the ordinary temperature with a current of $N.D_{100} = 0.05$ ampere and 2.7 volts. In 9 hours the bismuth will be fully precipitated and will not contain any copper.

10. From Gold. There is no recorded electrolytic separation of these metals.

11. From Iron. The acid solutions and conditions, given on pp. 75-78, will answer in this case. It may be remarked here that the deposition of bismuth from sulphuric acid solutions containing iron is attended with considerable difficulty. The iron present seems to exert an influence on the bismuth, tending to hold it in solution and prevent its deposition by the current. Especially is this true when the salt used is a ferric salt. This tendency of bismuth to be held in solution is shown even in a more marked degree when the liquid contains besides ferric alum an equal quantity of chrome alum. A current of 0.10 ampere will often not cause the slightest precipitation of bismuth. It was thought that this behavior of bismuth could be used to separate other metals from it. It was hoped that the bismuth would be held back by the iron and chrome alums and such metals as mercury, copper, and silver be deposited from the solution. These hopes were not realized. As soon as another metal is introduced the condition of affairs is changed, and both the metal and the bismuth are precipitated. Deposits of silver, however, were obtained containing but very little co-precipitated bismuth. Further investigation in this direction might lead to some very interesting and valuable results.

The best conditions for the separation of bismuth from iron were found to be as follows: To the bismuth solution containing 0.15 gram of bismuth and 1 c.c. of concentrated nitric acid, add 2 c.c. of sulphuric acid (sp. gr. 1.84), 0.5 gram of potassium sulphate, and a quantity of ferrous sulphate or ammonium ferric alum equivalent to 0.15 gram of iron. This solution should be

diluted to 150 c.c. and electrolyzed at a temperature of 45° C. If a ferrous salt is used, the current strength should be 0.03 ampere, but if a ferric salt is in solution, a higher current strength should be employed,—0.05 ampere,—the voltage in both cases being 2.0. In eight hours the deposition will be complete. The precipitated bismuth is free from iron (Kammerer).

In several cases the separation was made in the presence of urea nitrate, but its addition was no advantage.

RESULTS.

BISMUTH TAKEN.	BISMUTH FOUND.	IRON TAKEN.	UREA NITRATE.	POTASSIUM SULPHATE.	DILUTION.	SULPHURIC ACID.	TIME.	TEMPERATURE.	N.D.100.	VOLTS.	STYLE OF ANODE.
Grm.	Grm.	Grm.	Grm.	Grm.	C.c.	C.c.	Hours.	°C.	Amp.		
0.1434	0.1429	0.1500*	. .	0.5	150	2	8½	50	0.025	1.5	Spiral.
	0.1431	0.1500*	. .	0.6	150	2	7½	45	0.03	2	"
	0.1435	0.1500*	. .	0.5	150	2	24	45	0.03	2	"
	0.1430	0.1500*	. .	0.5	150	2	24	45	0.03	1.7	Basket.
0.1395	0.1394	0.1500*	0.5	0.2	150	2	8	45	0.035	2	"
	0.1400	0.1500*	0.5	0.2	150	2	8	50	0.035	2	Spiral.
	0.1393	0.1500*	0.5	0.2	200	2	8	45	0.05	2	Gauze.
	0.1397	0.1500†	. .	0.5	150	2	9	45	0.07	2	Spiral.
	0.1395	0.1500†	. .	1	150	2	9	45	0.06	2	"
	0.1394	0.1500†	. .	1	200	2	8	45	0.06	2	Gauze.
	0.1395	0.1500†	3.0	0.5	150	2	9	45	0.035	2	Spiral.

* Ferrous sulphate.

† Ferric ammonium sulphate.

12. From Lead. Experiments made in this laboratory (Jr. An. Ch., 7, 252) have demonstrated that the generally accepted statement that the metals could be separated in the presence of free nitric acid is not correct. The lead dioxide invariably contained bismuth. We are, therefore, for the present at least, without an electrolytic method for their separation.

- 13. From Magnesium.** The acid solutions and conditions given for the separation of bismuth from aluminium (p. 156) will serve to effect this particular separation.
- 14. From Manganese.** To the bismuth solution containing 0.1500 gram of metal and 1 c.c. of nitric acid (sp. gr. 1.42) add 3 c.c. of sulphuric acid (sp. gr. 1.84), 0.5 gram of potassium sulphate, and a quantity of manganous sulphate equivalent to 0.1500 gram of manganese. Dilute this solution to 150 c.c. with water and electrolyze with a current of $N.D_{100} = 0.025$ ampere and 2 volts, keeping the temperature at 45°C . The bismuth will be deposited in 9 hours in a beautiful form, free from manganese.
- At first the solution assumes a dark red color due to the oxidation of some of the manganese into permanganic acid. After an hour or two the color begins gradually to fade away and the solution again becomes colorless. A considerable quantity of hydrated oxide of manganese deposits on the anode during the electrolysis. This deposit was always examined for bismuth, but in no case was it found to contain any of this metal (Kammerer and Am. Ch. Jr., 8, 206).
- 15. From Molybdenum.** At present no electrolytic method is known for this purpose.
- 16. From Mercury.** See the separation of mercury from bismuth, p. 146.
- 17. From Nickel.** The directions recorded on p. 76 for the determination of bismuth in acid solutions may be followed with confidence in making this separation (Am. Ch. Jr., 8, 206; Jr. An. Ch., 7, 252; Z. f. anorg. Ch., 4, 270).
- 18. From Palladium and Platinum.** Separations are not known.

19. **From Potassium.** Follow the methods given for the determination of bismuth itself, pp. 75-78.
20. **From Selenium.** There is no existing electrolytic method.
21. **From Silver.** Freudenberg (*Z. f. ph. Ch.*, 12, 108) uses the nitrates of the two metals, adds to their solution several cubic centimetres of nitric acid of sp. gr. 1.2 and from 2 to 4 grams of ammonium nitrate, then electrolyzes with a current having a potential of 1.3 volts. The silver is precipitated through the night. The liquid containing the residual bismuth may be worked for the determination of the bismuth by the amalgam method, p. 75, although it would appear that Freudenberg always determined it by evaporation of the nitric acid solution and ignition of the residue, weighing finally bismuth oxide. The results obtained by him are:—

Silver used,	0.3790 gram ;	Bi = 0.3080 gram.
Silver found,	0.3793 “	Bi = 0.3073 “
Silver used,	0.2916 “	Bi = 0.3080 “
Silver found,	0.2914 “	Bi = 0.3072 “

22. **From Sodium.** Any one of the methods pursued in the determination of bismuth when alone will do for this purpose (pp. 75-78).
23. **From Strontium.** See the separation of barium from bismuth, p. 157.
24. **From Tellurium.** There is no recorded electrolytic separation.
25. **From Tin.** The solution contained 0.0518 gram of bismuth and 0.1031 gram of tin. To it were added 5 grams of tartaric acid and 15 c.c. of ammonium hydroxide, and the liquid then diluted to 175 c.c. with water

and electrolyzed at the ordinary temperature with $N.D_{100} = 0.02$ ampere and 1.8 volts, during the night (J. Am. Ch. S., 15, 204).

The chemist who proposed the preceding method also separated bismuth from a mixture of arsenic, antimony, and tin. The solution with which he operated contained 0.0518 gram of bismuth, 0.1009 gram of arsenic, 0.1024 gram of antimony, and 0.1031 gram of tin. To it were added 8 grams of tartaric acid and 3 c.c. of ammonia, then diluted to 175 c.c. with water and electrolyzed with a current of $N.D_{100} = 0.02$ ampere and 1.9 volts, at the ordinary temperature. The precipitation was made during the night. The time factor can probably be reduced by the application of a gentle heat. The bismuth precipitates rapidly and in an adherent form.

- 26. **From Tungsten.** There is no recorded separation.
- 27. **From Uranium.** The conditions presented on p. 76 for the determination of bismuth in sulphuric acid solution will serve excellently in making this separation (Am. Ch. Jr., 8, 206). See also bismuth from chromium.
- 28. **From Vanadium.** There is no recorded separation.
- 29. **From Zinc.** The conditions given in the determination of bismuth in nitric acid (p. 76), sulphuric acid (p. 76), and as amalgam (p. 75) will be found satisfactory in this separation (Am. Ch. Jr., 8, 206; Jr. An. Ch., 7, 255). See also bismuth from cobalt.

LEAD.

The importance of lead industrially makes not only its accurate determination of interest and value, but its separation from the metals frequently associated with it becomes a matter of deep concern. It will be generally conceded that lead is a metal that is best determined by the electrolytic procedure; this is vastly better than the ordinary gravimetric processes, and this, too, increases the value of its separations.

1. **From Aluminium.** As aluminium is not precipitated electrolytically from a nitric acid solution and the latter is especially well adapted for the deposition of lead in the form of its dioxide upon the anode, the conditions laid down upon p. 79 will be found to answer admirably in effecting the present separation.
2. **From Antimony.** A purely electrolytic procedure is at the present not known for the separation of these metals. In the *Ch. Z.*, 19, 1142 (1895), Nissenson and Neumann described a method for the analysis of an alloy of antimony and lead, which deserves attention here. It is not an electrolytic separation in any sense of that term, but a helpful suggestion.

The finely divided alloy is brought into solution with 4 c.c. of nitric acid (sp. gr. 1.4), 15 c.c. of water, and 10 grams of tartaric acid. Four cubic centimetres of concentrated sulphuric acid are added to the clear solution, which is then diluted with water, allowed to cool, and filled up to the mark of the $\frac{1}{4}$ -litre flask. On filtering from the lead sulphate, which has separated, the filtrate will contain all of the antimony. None will remain in the lead sulphate. Remove 50 c.c. of the filtrate with a

pipette, render it strongly alkaline with caustic soda, add 50 c.c. of a cold saturated sodium sulphide solution, boil, filter at once, wash and electrolyze the hot solution with a current of $N.D_{100} = 1.5-2.0$ amperes. An hour at the most will be required for the deposition of the antimony.

The lead sulphate should be digested for a few minutes with ammonia water. This changes it to hydroxide, which can be gradually introduced into a platinum dish containing 20 c.c. of nitric acid, in which it slowly dissolves. The liquid is then electrolyzed with the conditions indicated on p. 79.

3. **From Arsenic.** Neumann (Ch. Z., 20, 382) records his experience in attempting to separate these metals electrolytically, from which the conclusion may be deduced that in the presence of arsenic the lead determinations are not reliable. They are too low. When there is only a fraction of a per cent. of arsenic present, the results can be used, although the time then necessary for the complete precipitation of the lead as dioxide is prolonged to an unwarrantable degree. The experiments of Neumann were all conducted in nitric acid solution.
4. **From Barium, Strontium, Calcium, Magnesium, the Alkali Metals, Beryllium, Cadmium, Chromium, Iron, Uranium, Zirconium, Zinc, Nickel, and Cobalt** the separation of lead is easily made by observing the conditions given (p. 79) for its determination. There should be from 15 to 20 per cent. of concentrated nitric acid present. The liquid poured off from the deposit of lead peroxide is changed into the most favorable salt for the precipitation of the particular metal and the electrolysis proceeded with in the usual way.

5. **From Bismuth.** See p. 160.
6. **From Copper.** This separation has always been made in the presence of free nitric acid. The details of procedure are described under copper from lead, p. 129.
7. **From Gold.** This combination of metals has not received any attention, apparently, in the electrolytic way as the separation can be made more satisfactorily in other ways.
8. **From Manganese:—**

In nitric acid solution. It is well known that manganese can be precipitated from solutions in which the quantity of free nitric acid does not exceed from 3 to 5 per cent. Greater quantities of the acid prevent its appearance, its presence being made evident by the pink tinge of permanganic acid about the anode. As lead is completely deposited even in the presence of from 15 to 20 per cent. of acid, it would seem as if the separation could be made under the latter conditions. Until recently it has not been undertaken. Neumann recommends heating the solution containing the two metals and 20 per cent. of concentrated nitric acid to 70°, then electrolyzing with a current of from 1.5 to 2 amperes and 2.5 to 2.7 volts. It is absolutely essential to use hot solutions, strong currents, and not too large quantities of manganese (0.03 gram of manganese at the most in 150 c.c. of liquid). When large amounts are employed and the electrolysis prolonged the liquid will very probably become turbid, owing to the separation of dioxide of manganese (Ch. Z., 20, 383).

9. **From Mercury.** The details of this separation are given under mercury from lead, p. 152.
10. **From Selenium.** As selenium materially affects the

deposition of lead as dioxide from a nitric acid solution, it may be of interest to present some results from Neumann's experiments (Ch. Z., 20, 383). They are instructive and suggestive. He used solutions of lead nitrate containing sodium selenite. The first experiment was with lead alone, the others contain the two metals:—

LEAD PRESENT.	SELENIUM PRESENT.	NITRIC ACID.	LIQUID.	TIME.	AMPERES.	VOLTS.	LEAD FOUND.
0.2238	0.000	30 c.c.	150 c.c.	1 hr.	0.8	3	0.2238
0.2238	0.005	30 "	150 "	1 "	0.8	3	0.2208
0.2238	0.0100	30 "	150 "	1 "	0.8	3	0.2156
0.2238	0.0200	30 "	150 "	1 "	0.8	3	0.1886
0.2238	0.0500	30 "	150 "	1 "	0.8	3	0.0327

As the quantity of selenium was increased, the amount of lead dioxide deposited grew less. This was the case with lead and arsenic. The cathode also carried a deposit consisting of metallic lead and selenium.

11. From Silver:—

In nitric acid solution. An example, taken from a number made in this laboratory, will give the best conditions for carrying out this separation: To a solution containing 0.1028 gram of silver and lead equal to 0.0144 gram of dioxide were added 15 c.c. of nitric acid of 1.3 specific gravity. After dilution to 200 c.c. it was electrolyzed with a current of $N.D_{100} = 0.18$ ampere and 2.25 volts. The deposit of silver weighed 0.1023 gram and that of the dioxide 0.0144 gram. It is probably not necessary to say that the depositions were simultaneous and that the precautions described under the individual metals were carefully

observed. It must be borne in mind that silver quite often separates in the presence of nitric acid both as peroxide at the anode and as metal at the cathode, so that Luckow recommends the presence of at least 18 per cent. of nitric acid and also introduces several drops of oxalic acid, thus hindering the precipitation of silver dioxide (Jr. An. Ch., 7, 252; Z. f. ang. Ch., 1890, 345).

12. **From Tellurium.** This separation has not received any attention as yet.
13. **From Tin.** In this instance the usual gravimetric procedure is the preferable course to adopt in making the separation.

SILVER.

The current has proved a most valuable reagent in the separation of this metal from many others which occur associated with it. The ease and accuracy of these various separations recommend them.

1. **From Aluminium.** The conditions given on p. 81 for the precipitation of silver from a nitric acid solution will answer for this separation.
2. **From Antimony:—**
 - (a) *In ammoniacal solution.* In accordance with the suggestion of Freudenberg (Z. f. ph. Ch., 12, 109), if the antimony be raised to its highest state of oxidation it will only be necessary to add ammonium sulphate and ammonia water to the solution of the combined metals and electrolyze with a current having a pressure varying from 1.2 to 1.3 volts. The precip-

itated metal will not adhere well to the dish, so that the method will be used only when special reasons demand it.

- (b) *In acid solution.* To the nitric acid solution add tartaric acid, after having converted all the antimony into pentoxide, and electrolyze with a pressure not exceeding 1.4 to 1.5 volts. Freudenberg remarks that the deposit of silver is not well suited for weighing.
- (c) *In potassium cyanide solution.* The antimony should exist as pentoxide. After adding tartaric acid to the cyanide solution (1 gram of pure potassium cyanide for every 0.1 gram of metal), electrolyze with a pressure of from 2.3 to 2.4 volts.
3. **From Arsenic.** The methods just described for the separation of silver from antimony will be found applicable in this case (Am. Ch. Jr., 12, 428).
4. **From Barium.** Follow the instructions given on p. 81 for the determination of silver.
5. **From Bismuth.** See p. 162, bismuth from silver.
6. **From Cadmium:—**
- (a) *In nitric acid solution.* To the solution of the salts of the two metals add 15 to 20 c.c. of nitric acid of specific gravity 1.3, heat to 60°, and electrolyze with a current having a pressure of from 2 to 2.2 volts. The silver will be precipitated and should be treated as directed on p. 81. The acid filtrate can, by the addition of an excess of sodium acetate, be changed to a suitable form for the deposition of the cadmium. See p. 69.
- (b) *In potassium cyanide solution.* Add 2 grams of pure potassium cyanide to the solution, containing 0.1–0.2 gram of each metal, dilute to 125 c.c., heat to

65°–75°, then conduct a current of $N.D_{100} = 0.02-0.025$ ampere and 2.1 volts through the liquid. The silver will be completely precipitated at the expiration of from 4 to 5 hours. After removing the liquid from the precipitating dish it should be reduced in volume, introduced into a second weighed platinum dish, and electrolyzed as described on p. 68 for the deposition of the cadmium.

7. **From Calcium and Chromium.** See p. 168.
8. **From Cobalt.** An example will show the conditions which have been found very satisfactory in this particular separation: To the solution of the silver salt (0.1024 gram of silver) were added 0.1 gram of cobalt as nitrate and 2.75 grams of pure potassium cyanide. The liquid was diluted to 125 c.c. with water, heated to 65° C., and electrolyzed with $N.D_{100} = 0.038$ ampere and 2 volts. At the expiration of 5 hours the silver was completely deposited. It weighed 0.1027 gram. It contained no cobalt (J. Am. Ch. S., 21, 915). This procedure is preferable to the deposition of silver from a nitric acid solution.
9. **From Copper:—**
 - (a) *In nitric acid solution.* Freudenberg added 2 to 3 c.c. of nitric acid of 1.2 specific gravity to the solution of salts of the two metals, then electrolyzed with a pressure of 1.3–1.4 volts, and a current of 0.1 ampere. The silver was deposited free from copper (Z. f. ph. Ch., 12, 107; Berg-Hütt. Z. (1883), 375).

At the ordinary temperature this separation will require 7 hours, while at 60° the precipitation of the silver will be finished in 4 hours. The liquid siphoned off from the silver, after the addition of nitric acid, can be electrolyzed in a beaker glass in which a plati-

num cone is suspended. The copper is precipitated on the cone. A current ranging from 0.5 to 1.0 ampere will be required for this. The solution should be heated to 60°–65°.

The plan is ideal, but those who have attempted to repeat Freudenberg's work have encountered difficulties, and naturally modifications of the procedure have been proposed. Küster and v. Steinwehr (Z. f. Elektrochem., 4, 451), in particular, have made an exhaustive investigation of the precipitation of silver from nitric acid and its separation from copper in the presence of the latter acid. Their conclusion is briefly that the solution should contain from 1 to 2 c.c. of nitric acid (sp. gr. 1.4), and that to it should be added 5 c.c. of alcohol. Further, that the potential of the electrolyte should be kept constantly at 1.35–1.38 volts. An example will show how they operated: A weighed piece (0.3161 gram) of silver coin was dissolved in 2 c.c. of nitric acid (sp. gr. 1.4), the liquid was diluted to 150 c.c., 5 c.c. of alcohol were added, and the solution then heated to 55° and electrolyzed with 1.36 ± 0.01 volt. They obtained 0.2839 gram of silver = 89.83 per cent.

- (b) *In potassium cyanide solution.* This separation was first made by Smith and Frankel (Am. Ch. Jr., 12, 104) and has been carried out over a hundred times in this laboratory by experienced persons and by those who lacked experience, but in all cases the results have been most satisfactory.

Add 2 grams of pure potassium cyanide to the solution of mixed salts, heat to 65°, and electrolyze the liquid (125 c.c.) with a current of $N.D_{100} = 0.03\text{--}0.058$ ampere and 1.1–1.6 volts. The silver will be precipi-

tated in from 4 to 5 hours. It will, of course, be understood that if there be a great preponderance of copper over the silver the quantity of potassium cyanide will have to be increased. Example: A solution contained 0.1066 gram of silver and 0.5265 gram of copper. Four grams of pure potassium cyanide were added, the liquid was heated to 60° and electrolyzed for 3½ hours with a current of $N.D_{100} = 0.02 - 0.03$ ampere and 1.2 volts. The silver deposit weighed 0.1066 gram. The total dilution was 125 c.c.

The presence of three or four metals besides the silver also requires the addition of more alkaline cyanide (J. Am. Ch. S., 23, 582, also Brunck, Ber., 34, 1604; Revay, Z. f. Elektrochem., 4, 313).

10. **From Gold.** No successful method has yet been found. See Jr. An. Ch., 6, 87.
11. **From Iron.** When the iron is present as a ferrous salt in the mixture of salts, introduce into the solution 3 grams of potassium cyanide, dilute to 100 c.c. with water, heat to 65°, and electrolyze with a current of $N.D_{100} = 0.04$ ampere and 2.7 volts. The silver will be fully precipitated in 3 hours.

The separation of these metals can also be made in nitric acid solution by observing the conditions laid down on p. 81.

12. **From Lead.** Consult p. 167, where the separation of lead from silver is described.
13. **From Lithium.** See silver from barium and the alkaline earth metals, p. 169.
14. **From Magnesium.** See silver from barium, p. 169.
15. **From Manganese.** See lead from manganese, p. 166.
16. **From Mercury.** There is no known electrolytic

method for the separation of these metals. It is true that both can be precipitated from a nitric acid solution (pp. 72, 81), their joint weight be determined, after which the mercury can be expelled by heat and the silver residue be reweighed.

17. **From Molybdenum, Tungsten, and Osmium.** Follow the conditions recommended as satisfactory in the separation of silver from cobalt, p. 170.
18. **From Nickel.** Add 1.5 grams of pure potassium cyanide to the solution containing equal amounts of the metals (0.1–0.2 gram), dilute to 125 c.c. with water, heat to 60°–65°, and electrolyze with a current of $N.D_{100} = 0.02\text{--}0.03$ ampere and a pressure of 1.6–2.0 volts. The period of precipitation is usually three hours (J. Am. Ch. S., 21, 915).
19. **From Palladium.** The electrolytic separation of silver from palladium has not yet been made with any satisfaction.
20. **From Platinum.** To the solution of the combined metals add (for 0.2 gram of each metal) 1.25 grams of pure potassium cyanide, dilute to 125 c.c. with water, heat to 70°, and electrolyze with a current of $N.D_{100} = 0.04$ ampere and 2.5 volts. The precipitation will be complete at the end of 3 hours (J. Am. Ch. S., 21, 913).
21. **From Potassium, the other Alkali Metals, and Alkaline Earth Metals.** See the separation from barium, p. 169.
22. **From Selenium and Tellurium.** These separations have not yet been made in the electrolytic way.

Since this paragraph was written Meyer (Z. f. anorg. Ch., 31, 393) pursued a course in the determination of the atomic weight of selenium, in which he electrolyzed silver selenite in cyanide so-

lution. The silver was precipitated free from selenium, so that this method may be regarded as furnishing a satisfactory separation of the two metals. Perhaps tellurium can be similarly separated from silver.

- 23. From Tin.** When tin and silver are present together, digest their sulphides with ammonium sulphide, which will bring the tin into a proper condition to effect its determination electrolytically (p. 113). Dissolve the insoluble silver sulphide in nitric acid, and after the excess of the latter is expelled, add an excess of potassium cyanide and proceed as directed on p. 83. The silver will be deposited as a dense coating, and may be washed with hot water.

This same course, which is not a strict electrolytic procedure, has also been recommended for the separation of silver when associated with arsenic, antimony, and tin.

- 24. From Uranium.** See aluminium from silver, p. 168.
- 25. From Zinc.** Add 1 gram of pure potassium cyanide to the liquid containing at least 0.1 gram of each metal, dilute to 125 c.c. with water, and electrolyze at 70° with a current of $N.D_{100} = 0.032-0.038$ ampere and 2.76 volts. The silver will be fully precipitated in 3 hours. Treat as described on p. 83 (J. Am. Ch. S., 21, 915).

GOLD.

Separations of gold from certain metals have been carried out in the electrolytic way with marked success. As they may prove helpful, it was deemed advisable to describe them here in sufficient detail to make them generally applicable.

1. **From Antimony.** Add 0.5 to 1 gram of tartaric acid to their solution, followed by 3 to 4 grams of pure potassium cyanide; then electrolyze with the conditions given under the separation of gold from copper.
2. **From Copper.** The alkaline cyanide solution is best adapted for this separation. To the liquid containing 0.1665 gram of gold and a like amount of copper 4 grams of potassium cyanide were added. The solution was diluted to 250 c.c. with water, heated to 60°–65°, and electrolyzed with a current of $N.D_{100} = 0.05-0.08$ ampere and 1.7–1.9 volts. At the expiration of two and one-half hours 0.1667 gram of gold, free from copper, was precipitated. The liquid poured off from the gold, after the addition of an excess of ammonium carbonate, can be acted upon with a more powerful current and the copper be thus obtained (p. 65). See J. Am. Ch. S., 21, 921.
3. **From Cobalt.** In the early experiments made in the separation of these metals some difficulties were encountered, so that it will be necessary to follow the directions, given below, with the utmost care. After adding 4 grams of pure potassium cyanide to the solution, dilute to 125 c.c., heat to 65°, and electrolyze with a current of $N.D_{100} = 0.05-0.08$ ampere and 1.7–2 volts. Before interrupting the current introduce 1 c.c. of a 2 per cent. sodium hydroxide solution and increase the current to 0.10 ampere. The time necessary to effect this separation is usually 6 hours (J. Am. Ch. S., 21, 922).
4. **From Nickel.** Follow the conditions observed in the separation of gold from cobalt (see above).
5. **From Palladium.** To their solution add 2 grams of pure potassium cyanide, dilute to 150 c.c. with water,

heat to 65° , and electrolyze for 5 hours with a current of $N.D_{100} = 0.03$ to 0.06 ampere and 2.5 volts. The gold will be precipitated free from palladium.

6. **From Platinum.** Add to the solution, containing equal quantities of the two metals, about 1.5 grams of pure potassium cyanide, dilute to 250 c.c. with water, heat to 70° , and electrolyze for 3 hours with a current of $N.D_{100} = 0.01$ ampere and 2.7 volts (J. Am. Ch. S., **21**, 923).

7. **From Zinc.** In this separation the points to be observed are the quantity of potassium cyanide (4 grams), the current density, $N.D_{100} = 0.06$ ampere, and the pressure, which should be about 2.6 volts. The dilution and other conditions are similar to those followed in the separation of gold from copper, p. 175 (J. Am. Ch. S., **21**, 923).

It may be here stated that the conditions given for the separation of gold from copper will serve equally well for the separation of gold from molybdenum, tungsten, and osmium. The conditions observed in the precipitation of gold from a sulphaurate solution (p. 111) can be used with the certainty of good results in the separation of gold from arsenic, molybdenum, and tungsten, while its deposition from a phosphoric acid solution (p. 111) will prove of value in its separation from zinc and cobalt (Am. Ch. Jr., **13**, 206).

THE PLATINUM METALS.

The separations in this group of metals are not numerous. Platinum itself may be separated in an acid solution from zinc, cadmium, iron, nickel, and cobalt by

using a current of $N.D_{100} = 0.07-0.08$ ampere and 1.8–2.0 volts. Palladium can be separated from iridium by means of the method given on p. 106 for its determination. Platinum can be separated from iridium in a similar manner, with a current of $N.D_{100} = 0.05$ ampere and 1.2 volts (Classen). Although rhodium can be completely precipitated from an acid phosphate solution (p. 107), it cannot be thus separated from iridium.

● ANTIMONY, ARSENIC, AND TIN.

Under the metals which precede this group will be found the methods that experience has shown are best adapted for their separation from any one member of this group. So far as the latter itself is concerned, much credit is due Classen and his co-laborers for valuable data upon the electrolytic separation of its members.

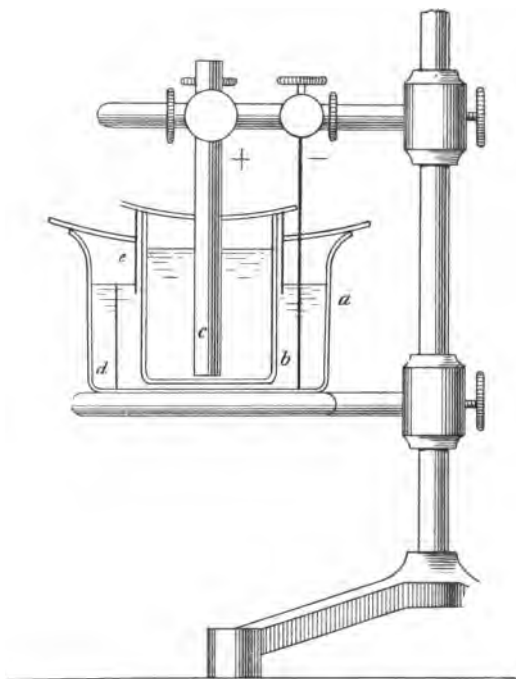
1. **Antimony from Arsenic.** The metals, or compounds of the same, are evaporated to dryness with aqua regia, the residue dissolved in 2 to 3 c.c. of water; concentrated sodium hydroxide is added so that there will be 2.5 grams of alkali present in the liquid and then 80 c.c. of sodium sulphide (sp. gr. 1.13–1.15) are introduced and the whole solution is diluted to 150 c.c., temperature $25^{\circ}-38^{\circ}$, and electrolyzed with $N.D_{100} = 1.5-1.6$ amperes and 2.1 volts (beginning) to 1.45 volts (at end). The time required for the separation of the antimony is usually 6 hours (Z. f. Elektrochem., 1, 291).
2. **Antimony from Tin.** The sulphides (or residue from a solution of the metals) are placed in a weighed platinum dish and covered with 80 c.c. of sodium sulphide

of specific gravity 1.13–1.15, to which are added 2 grams of sodium hydroxide. Dilute to 125 c.c. with water, heat to 57°–67°, and electrolyze with a current of $N.D_{100} = 1.45$ –1.50 amperes and 0.9–0.8 volt. The precipitation will be complete at the expiration of 2 hours (*Z. f. Elektrochem.*, 1, 291). Pour off the liquid into a second dish. Treat the deposit of antimony as previously directed (p. 115). To prepare the tin solution for electrolysis, proceed as described (p. 113) for the conversion of the sodium into ammonium sulphide (*Ber.*, 17, 2245; 18, 1110).

This separation has not always, in the hands of chemists, given the results that were confidently expected. There are disturbing features connected with it. It is not certain that these have been absolutely eliminated, although strenuous efforts have been put forth to arrive at such a result. Very recently Ost and Klapproth (*Z. f. ang. Ch.*, 1900, p. 827) conducted experiments in a cell provided with a diaphragm (p. 117). These demonstrated that by using a concentrated sodium sulphide solution the current, as a rule, mainly decomposes the sodium sulphide, and the antimony, if the bath pressure is low, does not participate in the electrolysis. It is precipitated as a secondary product by the sodium ion. When the pressure is great and the antimony salt assists in conducting the current, then the antimony wanders in the form of a complex anion, SbS_4 , to the anode. Disturbances also arise from the commingling of the anode and cathode liquids, so that these investigators have worked out the following piece of apparatus, to be used in this separation, which in their hands has yielded very satisfactory results. The sketch (Fig. 38) gives a perfect idea

of their scheme. *a* is a low beaker glass; the cylindrical diaphragm (a Pukall porous cell), *b*, stands in it. The anode is a rod of carbon, *c*, placed within the diaphragm-cell, while a bent sheet of platinum or a

FIG. 38.



platinum gauze, *d*, serves as cathode. The beaker and cell are covered with suitable cover-glasses. The diaphragm-cell above the liquid is covered with a suitable rubber ring, *e*, so that the drops of liquid falling from the cover-glass are returned to the cathode

chamber. The diaphragm, thoroughly cleaned, should always be preserved under water. The anode liquor should be introduced into the diaphragm-cell some time before the electrolysis begins and the apparatus should not be connected up until this liquor has penetrated through the walls of the diaphragm. During the electrolysis the level of the anode solution should stand from 0.5 to 1 cm. higher than that of the cathode solution. The anode chamber contains from 40 to 50 c.c., and the cathode chamber 150 c.c. The total volume of the electrolytes is about 150 c.c. The available surface of the cathodes equals 1 sqd m.

To illustrate the practical working of this idea, several results taken from Klapproth's doctoral thesis (*Die Fällung des Zinns und seine Trennung vom Antimon durch Elektrolyse*, Hannover, 1901) may here be incorporated:—

SEPARATION OF ANTIMONY AND TIN. DIAPHRAGM AND CARBON ANODE.

SOLUTION OF 90 C.C. IN CATHODE CHAMBER.			SOLUTION OF 50 C.C. IN ANODE CHAMBER.	TEMPERATURE.	CURRENT STRENGTH, IN AMPERES.	PRESSURE, IN VOLTS.	ANTIMONY FOUND, IN GRAMS.	DURATION OF PRECIPITATION (HOURS).
Na ₂ S, IN C.C.	Sb, IN GRAMS.	Sn, IN GRAMS.						
40	0.1500	0.2500	30 Na ₂ S	20°	0.08	0.9	0.1505	16
35	0.1500	0.2500	30 Na ₂ S	20°	0.19	1.10	0.1446	7
60	0.1500	0.5000	{ 20(NH ₄) ₂ S 30(NH ₄) ₂ SO ₄ }	20°	0.2	0.5	0.1500	16
40	0.3000	0.2500	{ 20(NH ₄) ₂ S 30(NH ₄) ₂ SO ₄ }	20°	0.15	1.2	0.2990	7
50	0.150	0.2500	{ 20(NH ₄) ₂ S 30(NH ₄) ₂ SO ₄ }	20°	0.5	1.0	0.1495	16

The solution, freed from antimony, can now be changed to one suitable for the precipitation of the tin by digesting it with ammonium sulphate (p. 113). If this is to be done in the absence of the diaphragm, then the latter must be removed from the solution, placed over the cathode beaker glass, and be washed for one-half hour, by allowing water to run through it. The liquid is later concentrated and electrolyzed (see p. 114).

But the tin may be estimated without removing the diaphragm. To this end the cathode liquor is reduced to a volume of 40 c.c. and the anode solution is renewed. The precipitation of the tin is then made at 70°. As much as 0.25 gram of the metal will be precipitated in from 2 to 3 hours. The pressure should not exceed 2 volts.

When antimony, arsenic, and tin are present together, expel the arsenic from their solution by the Fischer-Hufschmidt method (Ber., 18, 1110), and separate the antimony from the tin as already described on page 177.

In general analysis phosphoric acid is frequently precipitated as tin phosphate. The latter, of course, contains tin oxide. Dissolve the precipitate in ammonium sulphide. On electrolyzing the solution the tin will be precipitated, and the filtrate will contain all of the phosphoric acid; this can be estimated in the usual way (Classen). By observing this suggestion the determination of the phosphoric acid in a separate portion of the material will not be required.

**IRON, MANGANESE, NICKEL, ZINC, COBALT,
ALUMINIUM, CHROMIUM, AND PHOS-
PHORIC ACID.**

Electrolytic methods for the separation of these metals are neither so numerous nor so thoroughly worked out as with the metals already considered. Their separation from the heavy metals has been outlined under the same, and it only remains to describe the courses which may be pursued with this group of metals when present together.

1. Iron from Aluminium. Add sufficient ammonium oxalate to the solution of the salts of the metals (preferably not chlorides) so that it will contain from 2 to 3 grams of oxalate for each 0.1 gram of metal. Dilute to 175 c.c., heat to 40°, and electrolyze with $N.D_{100} = 1.95-1.6$ amperes and 4.3-4.4 volts. The iron will be precipitated in two and one-half hours (Ber., 18, 1795; 27, 2060; Z. f. Elektrochem., 1, 292). It is not advisable to allow the current to act longer than is necessary for the reduction of the iron. Towards the end of the electrolysis aluminium hydroxide is apt to separate and will coat the iron deposit. When the latter is dry, this adhering material can be removed with a handkerchief. The aluminium must be determined gravimetrically. The separation of aluminium hydroxide can be avoided if ammonium or potassium tartrate (1 gram) or citrate be added to the solution of the two metals, and it be heated to 60°, then electrolyzed with $N.D_{100} = 1$ ampere and 4-5 volts. It is true that the iron will probably contain small amounts of carbon.

These will not be excessive and will not affect the results seriously. See p. 100.

Drown and McKenna have endeavored to utilize the method described on p. 101 for the separation of iron from other elements. The conditions favorable for the deposition of the iron they found unfavorable for its separation from manganese. They experienced no difficulty in separating iron from aluminium or iron from phosphoric acid. It is expected that the process will give equally good results in the separation of iron and some other metals from titanium, zirconium, columbium, and tantalum (Wolcott Gibbs, *Am. Ch. Jr.*, **13**, 571). To determine iron in the presence of aluminium in steel they recommend the following procedure:—

“Dissolve 5–10 grams of iron or steel in sulphuric acid, evaporate until white fumes of sulphuric anhydride begin to come off, add water, heat until all the iron is in solution, filter off the silica and carbon, and wash with water acidulated with sulphuric acid. Make the filtrate nearly neutral with ammonia, and add to the beaker in which the electrolysis is made about 100 times as much mercury as the weight of iron or steel taken. The volume of the solution should be from 300 to 500 c.c. Connect with battery or dynamo in such a way that about 2 amperes may pass through the solution overnight. . . . When the solution gives no test for iron, it is removed from the beaker with a pipette while the current is still passing.” The aluminium is determined in this filtrate (*Jr. An. Ch.*, **5**, 627).

2. **From Chromium.** They can be separated in oxalate solution with conditions like those given above for the separation of iron from aluminium, the only difference being that the temperature should be about 65°

(Z. f. Elektrochem., 1, 292). The chromium during the electrolysis is converted into chromate. It must be determined gravimetrically. The second course, tartrate or citrate solution, also lends itself well to this separation. The requisites are given above under iron and aluminium. It may be added here that just as iron is separated in tartrate or citrate solution from aluminium and chromium, so can it also be separated from titanium.

3. **From Cobalt.** Classen (Ber., 27, 2060) adds about 8 grams of ammonium oxalate to the solution of the metals, dilutes with water to 120 c.c., heats to 65°–70°, and electrolyzes with $N.D_{100} = 1.6\text{--}2.0$ amperes and electrode pressure of 3.0–3.6 volts. The time required for complete deposition varies from 2 to 4 hours. The metals are precipitated together, their combined weight ascertained, then they are dissolved in acid, and the quantity of iron is found by titration. The cobalt is obtained by difference.

Vortmann suggests adding 3 to 6 grams of ammonium sulphate and a moderate excess of ammonium hydroxide to the solution of the metals, then electrolyzing with a current of $N.D_{100} = 0.4\text{--}0.8$ ampere and 4–5 volts. He remarks that by contact with the ferric hydroxide the deposit of cobalt will contain traces of iron, which can be fully eliminated by a second precipitation. (See iron from nickel.)

4. **From Manganese.** In considering this separation it should be remembered that objections have repeatedly been offered to the suggestion of Classen (Ber., 18, 1787); hence to obtain results at all satisfactory it is advisable to carry out the separation *exactly* as given by this chemist: "If a solution of the double oxalates of iron and manganese is subjected to electrolysis, without

the previous addition of a great excess of ammonium oxalate . . . it is impossible to obtain a quantitative separation of the two metals, because the manganese dioxide carries down with it considerable quantities of ferric hydroxide. The complete separation of the metals is possible only when the separation of the dioxide is delayed till most of the iron is precipitated." The electrolysis in the *cold* is not favorable; the large amount of ammonium carbonate, or ammonia formed in the decomposition of the excessive ammonium oxalate, dissolves the precipitated dioxide. "The rapid dissociation of ammonium oxalate when heated, however, gives a simple means of delaying, or entirely preventing, the formation of a manganese precipitate during the electrolysis." The solution containing the two metals is treated with 8 to 10 grams of ammonium oxalate and while hot (70°) is acted upon with a current of $N.D_{100} = 0.5$ ampere and 3.1–3.8 volts. Treat the iron deposit as directed on p. 99. Boil the liquid, poured off from the iron, with sodium hydroxide, to decompose the ammonium carbonate present, after which add sodium carbonate and a little sodium hypochlorite. The manganese is precipitated as dioxide, and after solution in hydrochloric acid is finally weighed as pyrophosphate.

Classen mentions that the method affords good results if the manganese content is not too high. In the analysis of ferromanganese, for example, it possesses no practical value (Ber., 18, 1787). Engels has tried to use the plan he describes for the deposition of manganese (p. 97) in effecting the separation of the latter from iron (Z. f. Elektrochem., 2, 414), but it has been observed that while the manganese was completely de-

posited as dioxide, it invariably contained as much as 0.02 gram of iron.

5. **From Nickel.** Classen deposits nickel and iron together (same as cobalt and iron) as an alloy, which is weighed, then dissolved in concentrated hydrochloric acid, the iron oxidized with hydrogen peroxide, and the ferric solution titrated with a stannous chloride solution. The current may vary from 1.75 to 2.2 amperes and the voltage from 3.4 to 4.0. The temperature of the liquid is usually 65°–70°. Two hours will be sufficient time for the precipitation of 0.2 gram of the combined metals.

Under iron from cobalt mention was made of a method which can be pursued in separating the metals now under discussion. To repeat, it consists in oxidizing the iron with bromine, then introducing into the solution from 3 to 6 grams of ammonium sulphate and a moderate excess of ammonium hydroxide. From this solution the nickel will be deposited in from 2 to 3 hours, with a current of $N.D_{100} = 0.4\text{--}0.8$ ampere. As in the case of the cobalt, traces of iron will appear in the nickel. This occlusion, so to speak, of iron has become a subject of discussion among those using electrolytic methods. Neumann (*Ch. Z.*, **22**, 731) remarks that it has tacitly been understood that the nickel carries down no iron with it. Indeed, Engels (*Thesis, Bern*) claims to have obtained perfectly correct results. Vortmann, as indicated, and also Ducru (*Ch. Z.*, **21**, 780; *C. r.*, **125**, 436; *B. s. Ch. Paris*, **17**, 1881) recommend the solution of the nickel and the determination of any iron present. So well satisfied is Ducru that he employs this method for the estimation of nickel in steel, asserting that the amount of enclosed iron is fairly constant (varying between 1 and 2 mg.), and that for

technical or commercial purposes it may be ignored. Neumann, on the other hand, maintains the absolute necessity of determining the amount of iron co-precipitated. In the analysis of nickel steel and nickel matte he proceeds as follows:—

Dissolve the substance in dilute sulphuric acid, and after a brief period introduce hydrogen peroxide into the solution to oxidize the carbon and the iron, thus obtaining a clear, yellow solution. Now add ammonium sulphate and ammonia, boil and continue the addition of ammonia to an excess, then dilute to a definite volume. Filter out 100 c.c. of this solution, mix with it ammonium sulphate and ammonia, dilute to 175–200 c.c., and electrolyze the hot liquid with $N.D_{100} = 1-2$ amperes and 3.4–3.8 volts. The electrolysis will be finished at the expiration of from $1\frac{1}{2}$ to 2 hours.

For another method by Vortmann applicable here, see zinc from nickel in the presence of Rochelle salt p. 189).

6. **From Phosphoric Acid.** If the iron has been precipitated from an oxalate solution (p. 99), from a citrate solution, or from an ammoniacal tartrate solution, the liquids poured off from the iron deposit will contain the phosphoric acid, which can then be removed as ammonium magnesium phosphate.
7. **From Titanium.** The method described on p. 100, with the conditions given there, will answer perfectly in making this separation.
8. **From Uranium.** (Ber., 14, 2771; 18, 2483.) In making this separation, follow the directions outlined on p. 99 for the separation of iron from aluminium. The uranium is precipitated in the form of hydroxide.
9. **From Zinc.** Add to the solution of the metals 1–3

c.c. of a solution of potassium oxalate (1:3) and 3 to 4 grams of ammonium oxalate and electrolyze the liquid with a current of $N.D_{100} = 1$ to 1.2 amperes. The zinc is deposited first, and no difficulty is experienced, providing its quantity is less than one-third that of the iron present. Classen provides for this condition by adding a weighed amount of pure ferrous ammonium sulphate in excess. Vortmann (*M. f. Ch.*, 14, 536) suggests two methods:—

(a) Add potassium cyanide to the solution of the metals until the precipitate formed at first has dissolved, then introduce sodium hydroxide. The iron is present in the solution as ferrocyanide, which in the presence of free alkali is not decomposed by the current. Avoid too large an excess of potassium cyanide, as it retards the separation of the zinc. The current should be $N.D_{100} = 0.3-0.6$ ampere.

(b) Several grams of Rochelle salt are introduced into the solution of the metals and then an excess of 10–20 per cent. sodium hydroxide, after which the electrolysis is conducted at 50°–60° with a current of $N.D_{100} = 0.07-0.1$ ampere and an electrode pressure of 2 volts.

1. **Cobalt from Manganese.** The course generally recommended for this separation is precisely like that given for the separation of iron from manganese. Owing to the great tendency of the manganese, toward the close of the decomposition, to separate out as dioxide which settles on the cobalt deposit, the method can hardly be regarded as being accurate.
2. **From Nickel.** To the acetic acid solution of the metals add 3 grams of ammonium sulphocyanide, 1 gram of urea, and from 1 to 2 c.c. of ammonia water to

neutralize the excess of acid. Warm the solution to 70° – 80° , and electrolyze with a current of $N.D_{100} = 0.8$ ampere and 1 volt. The time of precipitation is one and one-half hours. Nickel and sulphur pass to the anode, while the cobalt remains unprecipitated. The nickel should be dissolved in acid and reprecipitated according to the method described on p. 91, to obtain it pure. The liquid poured off from the first nickel deposit should be evaporated to dryness several times with nitric acid, the residue taken up in water, and the solution treated as directed on p. 93 (Balachowsky, C. r., 132, 1492; also M. f. Ch., 14, 548).

3. **From Zinc.** Add several grams of Rochelle salt and an excess of a dilute sodium hydroxide solution to the liquid containing the metals. Warm to 65° and electrolyze with $N.D_{100} = 0.3$ – 0.6 ampere and 2 volts. Usually there is a deposit upon the anode, hence it is advisable to previously weigh the latter and again at 110° after the precipitation is complete (Elektroch. Z., 1, 7).

1. **Nickel from Manganese.** What was said of the separation of cobalt from manganese applies here in every particular.
2. **From Zinc.** Add 4 to 6 grams of Rochelle salt to the solution of the two metals, then a concentrated solution of sodium hydroxide. Electrolyze the mixture with a current of $N.D_{100} = 0.3$ – 0.6 ampere. The precipitation of the zinc will be finished in a period of from 2 to 4 hours. Pour off the alkaline liquid, wash the zinc deposit with water and alcohol; dry at 100° C.

1. **Zinc from Manganese.** A solution contained 0.5074

gram of zinc sulphate and 0.1634 gram of manganese sulphate. To it were added 5 grams of ammonium lactate, 0.75 gram of lactic acid, and 2 grams of ammonium sulphate. It was diluted to 200 c.c. and electrolyzed at 20° – 25° C. with a current of $N.D_{100} = 0.24$ – 0.26 ampere and 3.7–3.9 volts. In 4 hours 22.786 per cent. of zinc was found, while theory required 22.78 per cent. (Riderer, J. Am. Ch. S., 27,789).

The writer would recommend the following course in separating the metals of this group: Separate the iron from the manganese, zinc, nickel, and cobalt, by precipitation with barium carbonate. Dissolve the iron precipitate in citric acid, and electrolyze the solution according to the directions given upon p. 100. The filtrate, containing the zinc, manganese, nickel, and cobalt, together with a little barium salt, is carefully treated with just sufficient dilute sulphuric acid to remove the barium. After filtering, electrolyze the filtrate in a platinum dish, connected with the anode of a battery, with a current of 0.3–0.5 ampere. A weighed piece of platinum foil will answer for the cathode. The manganese is deposited as dioxide (p. 96); the other metals remain dissolved and can only be separated by one of the usual gravimetric methods; or perhaps the suggestion of Vortmann (p. 189), for the separation of zinc from nickel and cobalt, would be applicable here, and these two might then be separated as outlined on p. 189. This course proved quite satisfactory in the analysis of the mineral franklinite, where, after having obtained the iron and manganese as described, the zinc was also determined electrolytically in the liquid poured off from the manganese deposit. If the solution containing these two

metals be very slightly acid with sulphuric acid, they can be precipitated simultaneously—the zinc at the cathode, and manganese dioxide at the anode.

URANIUM.

Smith has called attention to the separation of uranium in the electrolytic way from the alkali metals and from barium (p. 102). Actual results are given. It seemed desirable to amplify the suggestion; hence the presentation of the results given below. It may be said here, that in attempting to separate uranium from nickel and cobalt no satisfaction could be obtained, so that eventually that particular line of experiment was abandoned. During the precipitation of the urano-uranic hydrate the dish should be well covered so that as little evaporation as possible occurs. It was observed that in case of evaporation there was danger of other salts separating upon the exposed metal, and on refilling with water the uranium precipitate was apt to enclose the same and thus carry with it a slight impurity. This precaution is especially necessary in the separation from zinc (J. Am. Ch. S., 23, 608).

I. FROM BARIUM (ACETATES).

	U ₃ O ₈ PRESENT, IN GRAMS.	BARIUM PRESENT, IN GRAMS.	29 PER CENT. FREE ACETIC ACID, C.C.	DILUTION. C.C.	TEMPERATURE. °C.	CURRENT.	VOLTS.	TIME. HOURS.	U ₃ O ₈ FOUND, IN GRAMS.	ERROR, IN GRAMS.
1	0.1116	0.11	0.5	125	70	N.D. ₁₀₇ = 0.02 A	2	5 ³⁰	0.1119	+0.0003
2	0.1116	0.11	0.5	125	65	N.D. ₁₀₇ = 0.04 A	8	5 ³⁰	0.1117	+0.0001
3	0.1116	0.11	0.2	125	70	N.D. ₁₀₇ = 0.1 A	4.5	4	0.1117	+0.0001

2. FROM CALCIUM (ACETATES).

	U ₂ O ₃ PRESENT, IN GRAMS.	CALCIUM PRESENT, IN GRAMS.	29 PER CENT. FREE ACETIC ACID C.C.	DILUTION. C.C.	TEMPERATURE. °C.	CURRENT.	VOLTS.	TIME. HOURS.	U ₂ O ₃ FOUND, IN GRAMS.	ERROR, IN GRAMS.
1	0.1116	0.1	0.2	125	70	N.D. ₁₀₇ = 0.025 A	2.25	6½	0.1113	-0.0003
2	0.1116	0.1	0.2	125	70	N.D. ₁₀₇ = 0.04 A	2.2	5½	0.1114	-0.0002
3	0.1116	0.1	0.2	125	70	N.D. ₁₀₇ = 0.05 A	2.25	4½	0.1113	-0.0003
4	0.1116	0.1	0.2	125	70	N.D. ₁₀₇ = 0.025 A	2.0	4½	0.1115	-0.0001

3. FROM MAGNESIUM (ACETATES).

	U ₂ O ₃ PRESENT, IN GRAMS.	MAGNESIUM PRESENT, IN GRAMS.	29 PER CENT. FREE ACETIC ACID. C.C.	DILUTION. C.C.	TEMPERATURE. °C.	CURRENT.	VOLTS.	TIME. HOURS.	U ₂ O ₃ FOUND, IN GRAMS.	ERROR, IN GRAMS.
1	0.1116	0.1	0.1	125	70	N.D. ₁₀₇ = 0.026 A	2.25	6	0.1115	-0.0001
2	0.1102	0.1	0.1	125	70	N.D. ₁₀₇ = 0.05 A	2.25	5½	0.1104	+0.0002
3	0.1120	0.1	0.1	125	75	N.D. ₁₀₇ = 0.15 A	4.0	4	0.1119	-0.0001

4. FROM ZINC (ACETATES).

	U ₂ O ₃ PRESENT, IN GRAMS.	ZINC PRESENT, IN GRAMS.	29 PER CENT. FREE ACETIC ACID. CC.	DILUTION. C.C.	TEMPERATURE. °C.	CURRENT.	VOLTS.	TIME. HOURS.	U ₂ O ₃ FOUND, IN GRAMS.	ERROR, IN GRAMS.
1	0.1120	0.1	0.1	125	70	N.D. ₁₀₇ = 0.021 A	2.25	6	0.1120	...
2	0.1102	0.2	0.2	125	70	N.D. ₁₀₇ = 0.017 A	2.25	6	0.1099	-0.0003
3	0.1102	0.1	0.1	125	70	N.D. ₁₀₇ = 0.02 A	2.2	6	0.1100	-0.0002
4	0.1102	0.1	0.1	125	75	N.D. ₁₀₇ = 0.025 A	4.4	4½	0.1103	+0.0001
5	0.1102	0.15	0.2	125	75	N.D. ₁₀₇ = 0.01 A	2.2	6	0.1105	+0.0003
6	0.1102	0.2	0.2	125	75	N.D. ₁₀₇ = 0.02 A	2.25	6	0.1099	-0.0003

3. DETERMINATION OF THE HALOGENS IN THE ELECTROLYTIC WAY.

LITERATURE.—Whitfield, *Am. Ch. Jr.*, 8, 421; Vortmann, *Elektroch. Z.*, 1, 137; 2, 169.

Whitfield proceeds as follows: The silver halide is collected in a Gooch crucible and dried directly over a low Bunsen flame. After weighing it is dissolved by introducing the crucible and asbestos into a concentrated potassium cyanide solution. The silver is then deposited in a platinum dish of 100 cm² surface with a current of 0.07 ampere. It is not advisable to work with more than 2 grams of silver halide.

Vortmann has developed an electrolytic scheme for the direct determination of the halogens. As he has given the most attention to iodine, its method of estimation will be presented here.

To the aqueous solution of potassium iodide were added several grams of Seignette salt and 16–20 c.c. of a 10 per cent. solution of sodium hydroxide. The liquid was then diluted to 150 c.c. and placed in a crystallizing dish or in a platinum dish. If the first was used, then a platinum disc, 5 cm. in diameter, was made the cathode, whereas in the second instance the dish itself became the cathode, the anode being a circular plate of pure silver, 5 cm. in diameter, or a plate of platinum of like size, coated with silver. The electrolysis was made with a current of 0.03–0.07 ampere and 2 volts. It was found expedient, after several hours, to replace the anode coated with silver iodide with another, and the electrolysis was continued

until the anode ceased to increase in weight. This change in anodes is absolutely necessary when the quantity of iodine exceeds 0.2 gram. The iodine may exist as iodide or iodate. The alkaline tartrate is introduced to prevent the silver iodide from becoming detached.

4. DETERMINATION OF NITRIC ACID IN THE ELECTROLYTIC WAY.

LITERATURE.—Vortmann, Ber., 23, 2798.

To the solution of the nitrate, in a platinum dish, add a sufficient quantity of copper sulphate. Acidulate the liquid with dilute sulphuric acid and electrolyze with a current of 0.1 to 0.2 ampere. When the deposition of the copper is completed, pour off the liquid, reduce it to a small volume, and distil off the ammonia in the usual manner. The quantity of copper sulphate added should be determined by the quantity of nitric acid present. If potassium nitrate is the salt undergoing analysis, add half of its weight in copper sulphate.

5. OXIDATIONS BY MEANS OF THE ELECTRIC CURRENT.

LITERATURE.—Smith, Ber., 23, 2276; Am. Ch. Jr., 13, 414; Frankel, Ch. News, 65, 64.

When natural sulphides, *e. g.*, chalcopyrite, marcasite, etc., are exposed to the action of a strong current in the presence of a sufficient quantity of potassium hydroxide, their sulphur will be quickly and fully oxidized to sul-

phuric acid (Jr. Fr. Ins., April, 1889; Ber., 22, 1019). The metals (iron, copper, etc.) originally present in the mineral separate as oxides and metal on dissolving the fused alkaline mass in water. This method of oxidation eliminates many other disagreeable features of the old methods. Its rapidity and accuracy entitle it to the following brief description:—

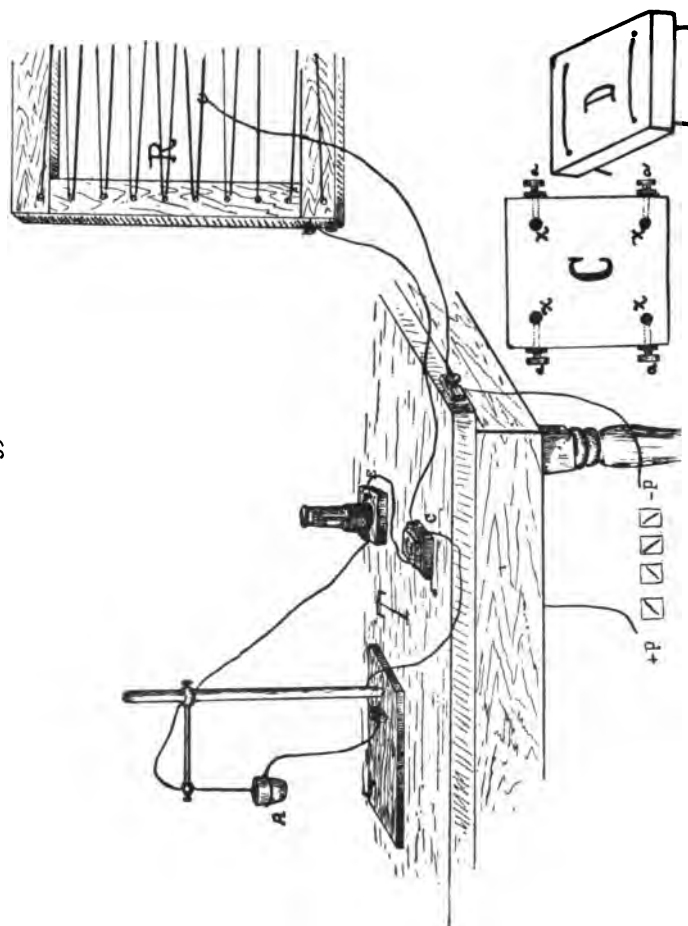
Place about 20 grams of caustic potash in a nickel crucible $1\frac{1}{4}$ inches high and $1\frac{3}{8}$ inches wide. Apply heat from a Bunsen burner until the water has been almost entirely expelled, when the flame is lowered so that the temperature is just sufficient to retain the alkali in a liquid condition. The crucible is next connected with the negative pole of a battery, and the sulphide to be oxidized is placed upon the fused alkali. As some natural sulphides part with a portion of their sulphur at a comparatively low temperature, it is advisable to allow the alkali to cool so far that a scum forms over its surface before adding the weighed mineral.

The heavy platinum wire, attached to the anode, extends a short distance below the surface of the fused mass. When the current passes, a lively action ensues, accompanied with some spattering. To prevent loss from this source, always place a perforated watch crystal over the crucible. After the current has acted for 10–20 minutes, interrupt it. When the crucible and its contents are cold, place them in about 200 c.c. of water, to dissolve out the excess of alkali and alkaline sulphate. Filter. Invariably examine the residue for sulphur by dissolving it in nitric acid and then testing with barium chloride. The alkaline filtrate is carefully acidulated with hydrochloric acid, and after digesting for some time is precipitated with a boiling solution of barium chloride. When the hydro-

chloric acid is first added, care should be taken to observe whether hydrogen sulphide or sulphur dioxide is liberated. If the oxidation is incomplete sulphur also makes its appearance as a white turbidity. The caustic potash employed in these oxidations should always be examined for sulphur and other impurities. As it is difficult to obtain alkali perfectly free from sulphur compounds, a weighed portion should be taken and its quantity of sulphur deducted from that actually found in the analysis.

The arrangement of apparatus employed in the oxidations just outlined is represented in Fig. 39. The crucible *A* is supported by a stout copper wire bent as indicated, and held in position by a binding screw attached to the base of a filter stand. The arm of the latter carries a second binding screw holding the platinum anode in position. While the platinum rod is generally the positive electrode, it is best to make it the negative pole for at least a part of the time during which the current acts. This is advisable because in many of the decompositions metals are precipitated upon the sides of the crucibles, and can readily enclose unattacked sulphide, so that by reversing the current (the poles) any precipitated metal will be detached, and the enclosed sulphide be again brought into the field of oxidation. Cinnabar is a sulphide which has a tendency to mass together, and it could only be decomposed and its sulphur thoroughly oxidized by reversing the current every few minutes. To reverse the current use the contrivance *C*; this is nothing more than a square block of wood fastened to the top of the table, *T*, by a screw or nail. The four depressions (*x*) in it contain a few drops of mercury, into which the side binding screws (*a*) project. The mercury cups are made to communicate with each other by a cap of wood, *D*, carrying two

FIG. 39.



wires, which pass through it and project a slight distance on its lower side. By raising the cap and turning it so that the wires are vertical ($\uparrow$) or horizontal ($\rightarrow$), the crucible or the platinum wire extending into the fused mass can be made the anode or cathode in a few seconds. E is a Kohlrausch amperemeter (Fig. 20) and R the resistance frame (Fig. 18).

Storage batteries furnish the most satisfactory current for work of this character. In the sketch the cells stand beneath the table; the wire from the anode passes through a hole in the table-top, and is attached to one of the binding-posts of the block C , while the positive wire is attached to a binding-post at the end of the table-top, and from here it passes to the resistance frame, R , where it is fixed by an ordinary metallic clamp.

For most purposes the strength of current need not exceed 1–1.5 amperes; however, it may be necessary occasionally to increase it to 4 amperes. Pyrite, FeS_2 , is even then not completely decomposed. This particular case requires the addition of a quantity of cupric oxide equal in weight to the pyrite and a current of the strength last indicated before all of its sulphur is fully converted into sulphuric acid.

By increasing the number of crucibles it will be possible to conduct at least from four to six of these decompositions simultaneously, and by using a volumetric method of estimating the sulphuric acid, a sulphur determination can easily be executed in forty minutes.

Experience has demonstrated that 0.1–0.2 gram of material will require about 20–25 grams of caustic potash.

Dr. Lee K. Frankel has conclusively demonstrated that the arsenic contained in metallic arsenides, *e. g.*, arsenopyrite, rammelsbergite, etc., can be entirely converted into

arsenic acid by the above method. He recommends conditions analogous to those employed with the sulphides.

The current will also completely decompose the mineral chromite. For a quantity of material varying from 0.1–0.5 gram use from 30–40 grams of stick potash and a crucible slightly larger than that recommended in the oxidation of sulphides and arsenides. The current should not exceed one ampere. Thirty minutes will be sufficient for the oxidation. At the expiration of this period allow the mass to cool, take up in water, filter off from the iron oxide, acidulate the filtrate with sulphuric acid, add a weighed quantity of ferrous ammonium sulphate, and determine the excess of iron with a standardized bichromate solution, using potassium ferricyanide as an indicator. Upon oxidizing 0.4787 gram of chromite by the above process 51.77 per cent. of chromic oxide was obtained, while a second sample of the same mineral, oxidized by the Dittmar method, gave 51.70 per cent. of chromic oxide. If the chromium be estimated volumetrically, the chromium content in a chrome ore may be ascertained in less than an hour.

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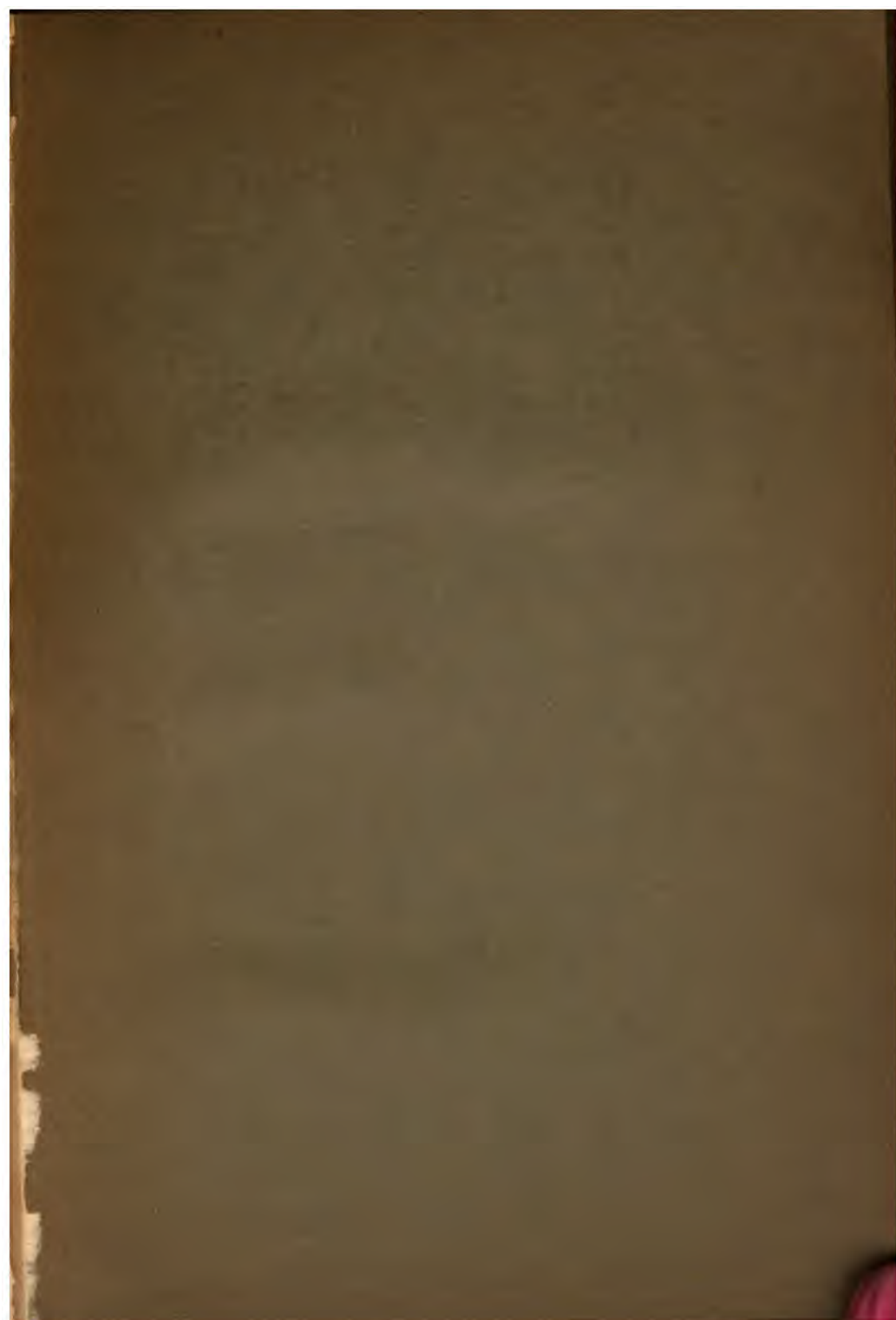
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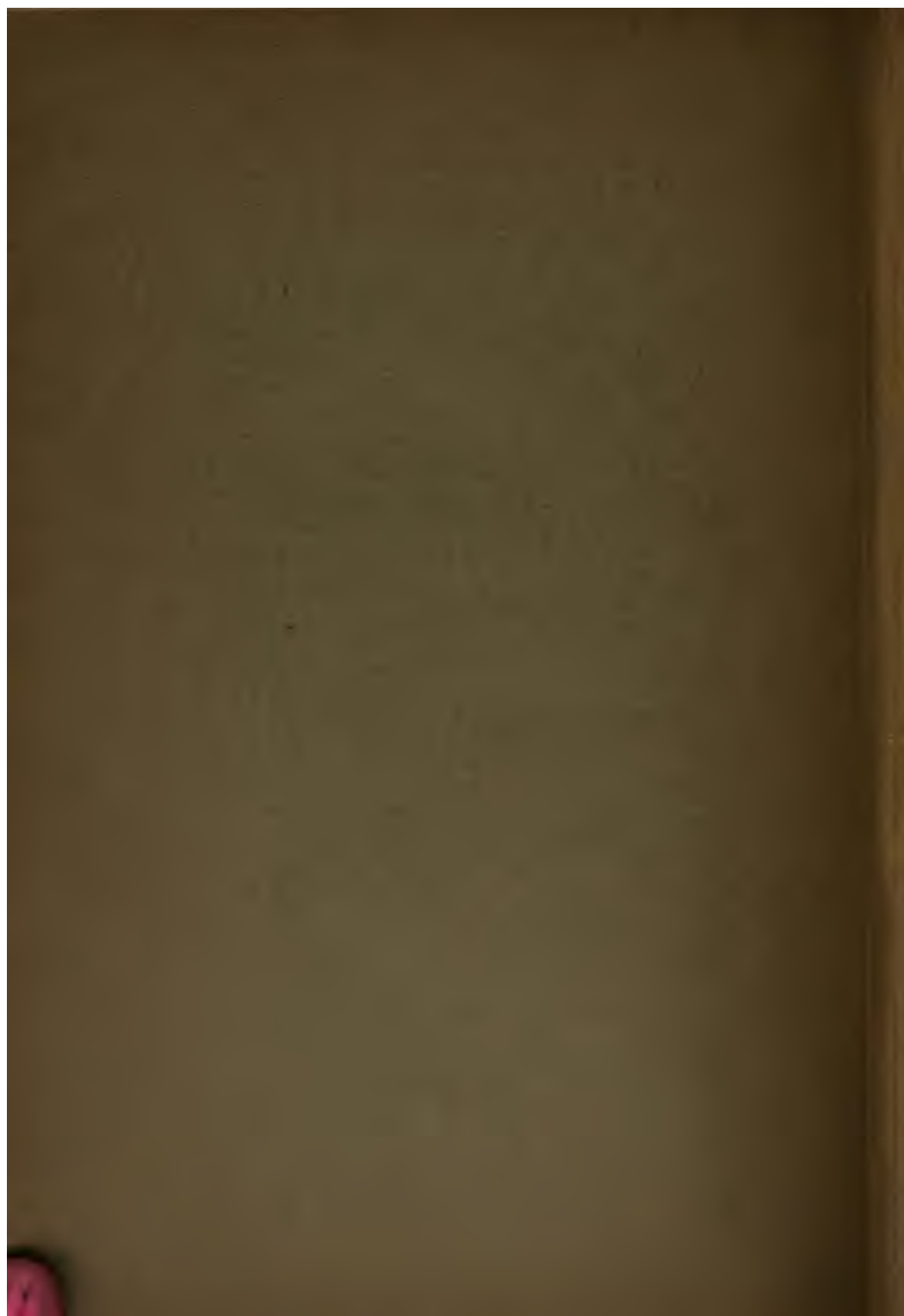
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